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Volatile Corrosion Inhibitors and Boiler Water Additives: Potential for Nitrosamine Formation. Task III. Chemical Technology and Economics in Environmental Perspectives

Midwest Research Inst.
Kansas City, MO

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16. ABSTRACT

Study investigated volatile corrosion inhibitors (VCIs) and the use of amines as boiler water additives. The major VCI's are dicyclohexylammonium nitrite (Dichan), "nonnitrite" Dichan substitutes, and benzotriazole. The present market is about 310,000 kg/year; over 90% of the use is in the preparation of impregnated paper and other wrapping materials. Dichan can be converted to the corresponding nitrosamine; commercial products can contain up to 1 ppm of the nitrosamine. Nonnitrite substitutes are less likely to be converted to nitrosamines but can likely be readily nitrosated under environmental conditions. Benzotriazole is likely to be environmentally stable and not converted to the corresponding nitrosamine. Population exposure to VCI's is large since it is estimated that over 20 million individual items are wrapped in VCI impregnated paper. Two cases of nitrosamine detection at levels of 100 and 90 ppm in VCI wrapping paper have been reported. A number of amines are employed for treating boiler water. The total market in 1978 was estimated to be 9,000 to 10,300 metric tons. The two most widely used neutralizing amines are cyclohexylamine and morpholine; octadecylamine is the most common film-forming amine. There is no experimental evidence to indicate whether or not nitrosamines are formed in boilers as a result of the addition of these amines. Picogram amounts of N-nitrosomorpholine were recently reported in the steam condensate from boilers and at several other locations at a plant which produces chemicals for the rubber industry. It was speculated that a transnitrosation reaction of morpholine with N-nitrosodiphenylamine may have resulted in the N-nitrosomorpholine.

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TASK III - VOLATILE CORROSION INHIBITORS AND BOILER WATER ADDITIVES: POTENTIAL FOR NITROSAMINE FORMATION

by

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For

Environmental Protection Agency
Office of Pesticides and Toxic Substances
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The report was prepared as part of a preliminary evaluation by EPA and should not be construed as presenting final Agency judgement concerning the subject chemicals.

PREFACE

This report presents the results of a study to develop information concerning volatile corrosion inhibitors.

This study was performed by Midwest Research Institute, as Task III under Contract No. 68-01-3896 for the Office of Pesticides and Toxic Substances of the U.S. Environmental Protection Agency. The project officer for this study was Mr. Roman Kuchkuda. Mr. Charles Auer was the EPA Technical Officer. Principal Midwest Research Institute contributors to this study included: Dr. Alfred F. Meiners (Task Leader), Principal Chemist; Mr. Howard Gadberry, Senior Advisor for Technology; Ms. Bonnie L. Carson, Associate Chemist; Mr. Harold P. Owens, Associate Industrial Chemist; Ms. Mary Simister, Social Analyst; Ms. Joy McCann, Junior Scientist; and Mr. Fred Hopkins, Assistant Scientist. Dr. Thomas W. Lapp is the project leader for this contract, under the supervision of Dr. Edward W. Lawless, Chemical Impact Assessment Section.

Approved for:

MIDWEST RESEARCH INSTITUTE

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for B. W. Macy, Acting Director
Center for Technoeconomic Analysi

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SECTION 1

INTRODUCTION AND OBJECTIVES

The Environmental Protection Agency (EPA) has expressed concern that potentially carcinogenic nitrosamines may be formed from the use of secondary amines* as components of volatile corrosion inhibitors (VCIs). Recent reports have shown that nitrosamines are formed when secondary amines are incorporated into plastic wrapping materials for metal products. Nitrosamines have also been detected in commercial samples of similar wrapping materials. Recent reports have stated that substitutes are being developed for these products because of the nitrosamine problems. Relatively large quantities of volatile amines are also known to be used as boiler water additives. Another concern was the possible use of amines in boilers with nitrate or nitrite salts, thereby resulting in the potential for nitrosamine formation.

This study was initiated to provide information concerning the materials which are used for these purposes, the quantities which are consumed, and the possibilities for nitrosamine formation.

According to most industry sources, the term "volatile corrosion inhibitor" refers to compounds that can volatilize and protect metal surfaces exposed to air or other corrosive gases. It might be more accurate to describe VCI as "vapor phase corrosion inhibitors." Relatively few compounds can function as true VCIs, and almost all of these are secondary amine derivatives; however, hundreds of other compounds (including a wide variety of amines) are used in corrosion protection applications where a degree of volatility may be desirable.

Chemicals which are commonly used as VCIs are not normally used as boiler water additives. A number of secondary amines and other volatile compounds are employed as neutralizing agents and film-forming materials in the treatment of boiler water. Thus, the primary function of the boiler water amines is distinctly different from VCIs. The volatility of the boiler water amines, specifically their ability to steam distill, simply allows them to be introduced into the boiler and transferred through the system to the area which requires corrosion protection, i.e., the area where the steam condenses to give a liquid-metal interface.

This report is divided into four major sections. Section 1 presents an introduction to the report and outlines the program objectives. Section 2

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* A secondary amine has two organic groups and one hydrogen atom attached to the nitrogen atom (R_1R_2NH).

contains a summary and conclusions. Section 3 provides data concerning VCIs. Section 4 presents a discussion of the use of volatile amines in boiler systems. There are four appendices: Appendix A contains descriptions of the physical properties of VCIs, boiler water amines, and related compounds; Appendix B reviews the overall market for amines as VCIs; Appendix C reviews possible nitrosamine formation reactions of VCIs and boiler water amines; and Appendix D contains available market information on VCIs, boiler water amines, and related products. This information was obtained from nonconfidential information submitted to EPA by manufacturers and importers as of January 1979.

SECTION 2

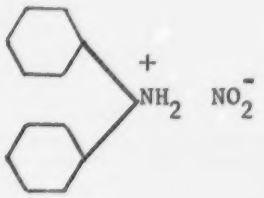
SUMMARY AND CONCLUSIONS

A summary of the results obtained in this study is presented in this two-part section. The first part summarizes the investigation of VCIs, and the second part summarizes the study of the use of amines in boiler systems.

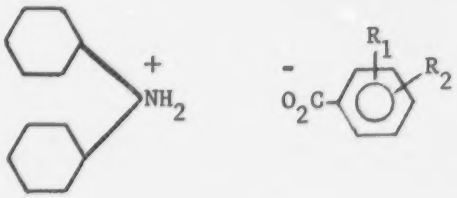
VOLATILE CORROSION INHIBITORS

The semantics of VCIs is not totally clear, but the term is generally recognized to mean a chemical substance that by virtue of its volatility at room temperature reaches a metal surface in need of corrosion protection.

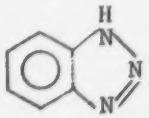
Although a large number of volatile products have been used as VCIs in the past, the major products at present are dicyclohexylammonium nitrite (Dichan), "nonnitrite" substitutes for Dichan (in which the nitrite has been replaced), and benzotriazole.



Dichan (Dicyclohexylammonium nitrite)



"Nonnitrite" Dichan substitute (substituted benzoate salt of dicyclohexylamine)



Benzotriazole

Industry sources indicate that Dichan has recently been substantially replaced by nonnitrite VCIs. The structures of these products are proprietary, but apparently they are salts of dicyclohexylamine, probably substituted benzoic acid salts in which the substituted benzoate ion has replaced the nitrite ion of Dichan.

Benzotriazole is a VCI which inhibits the corrosion of copper. As a VCI, it is used almost exclusively in impregnated paper. Benzotriazole has many applications other than as a corrosion inhibitor; most of the production quantities in the United States are probably used in photographic processes.

Market Information

The present market for VCI products is approximately 310,000 kg/year (Table 2-1) and appears to have remained at this level for the last few years. The products have been on the market in the United States for at least 25 years but have never substantially exceeded the present volume.

TABLE 2-1. U.S. MARKET FOR VCI PRODUCTS, 1978

Compounds	Amount of VCI used (x 10^3 kg/yr)	
	Impregnated paper and other wrapping materials	All other VCI applications
Dichan (dicyclohexyl-ammonium nitrite	95	14
Benzotriazole	30	0
"Nonnitrite" VCIs	170	2
Totals	295	16

Source: MRI estimates.

Uses

Over 90% of the use of these products is in the preparation of impregnated paper and other wrapping materials. Impregnated paper is widely used for the protection of small metallic objects during storage and shipment. Impregnated paper is also used to protect relatively large items, for example, stacks of black plate (untinned steel) and tin plate used in the manufacture of cans. A relatively new VCI product on the market is an impregnated plastic film for wrapping.

VCIs are also used in applications in which the solid product is placed within the item it is designed to protect. Many "devices" have been developed

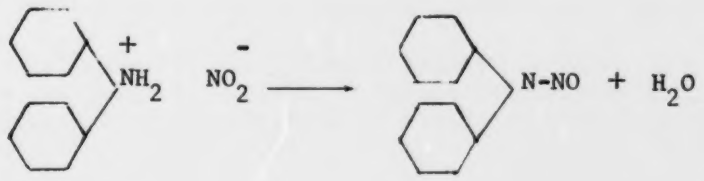
for this purpose. Formerly, the products were used to protect equipment within the holds of cargo vessels during shipment, but this application has apparently greatly declined or even disappeared.

Mechanism of Action

Although the mechanism of VCI inhibition has not been studied in detail, the protection is apparently due to adsorption of a film on the metal surface. This film protects against the corrosive effects of water and/or oxygen.

Nitrosamine Formation Potential

Dichan, the nitrite salt of dicyclohexylamine, can apparently be converted under ambient conditions to the corresponding nitrosamine. The commercial product can contain significant concentrations (1 ppm) of the nitrosamine.



Dichan N-Nitrosodicyclohexylamine

The nonnitrite VCIs are less likely to be converted to nitrosamines because the nitrite salt, a major nitrosating reagent, is not available. However, other secondary amines can be nitrosated under "environmental" conditions via a number of mechanisms, and the nonnitrite VCIs would be expected to be readily susceptible. (See Nitrosamine Formation Reactions, Appendix C.)

Potential for Adverse Environmental Effects

A large number of people come into contact with VCIs because of their use in the wrapping of small metallic items. Over 20 million individual items are wrapped each year in VCI paper (MRI estimate) and these packages ultimately expose the user to VCI vapor. Production workers involved in the manufacture of VCIs and VCI-impregnated paper are also exposed. Two cases of nitrosamine detection in VCI wrapping material have been reported. In one, N-nitroso-N,N-dibutylamine was found at an estimated concentration of 100 ppm in an unidentified commercial film. The same researchers prepared a VCI polyethylene film and found it to contain 90 ppm nitrosomorpholine.

Dichan enters the atmosphere as a VCI, but it probably is not a long-lived constituent because of its susceptibility to photolysis. However, no reports were found concerning the nature of its photolytic decomposition products.

No reports have been found concerning the environmental effects of stability in the environment of nonnitrite Dichan substitutes. Dichan substitutes can probably be nitrosated in the environment via a number of mechanisms.

Benzotriazole--

Benzotriazole is likely to be quite stable and persistent in the environment. However, the perceived potential for environmental contamination has been small, and the attention paid to it has been negligible. Benzotriazole apparently cannot be converted to the N-nitroso product.

VOLATILE AMINES IN BOILER SYSTEMS

A number of amines are employed in the treatment of boiler water; the amines are primarily used as neutralizing agents and film-forming materials. Thus, their primary function in these applications is distinctly different from that of true VCIs. Their volatility (or more exactly, their ability to steam distill) simply allows them to be introduced into the boiler and transferred through the system to the area which requires corrosion protection, namely, the area where the steam condenses to form a liquid-metal interface.

The most widely used neutralizing amines are cyclohexylamine, morpholine, 2-diethylaminoethanol, methylpropylamine (relatively new), and a few others. The total annual market is estimated to be 6,500 to 7,800 metric tons in 1978 (see Table 2-2).

Octadecylamine represents about 95% of the film-forming amine market, estimated to be about 5 million pounds in 1978.

Potential for Nitrosamine Formation in Boilers

There is no experimental evidence to indicate whether or not nitrosamines are formed in boilers as a result of the addition of boiler water amines. Most boilers are operated under conditions which would (a) limit the possibility for nitrosamine formation and (b) probably result in the destruction of any nitrosamine that might be formed. However, under certain circumstances, the possibility for nitrosamine formation is conceivable. These possibilities are discussed in the following paragraphs.

Modern High-Pressure Boilers--

Nitrates and nitrites are potential nitrosating agents for boiler water amines. However, neither nitrates nor nitrites are ordinarily added to boiler water. For high-pressure boilers such as those used by electric utilities, high-purity water is essential. Purification procedures include the careful removal of dissolved solids including nitrates, present at the 1 to 10 ppm level in most untreated waters. Some purification procedures require deionization of the water, and this process would remove nitrate and nitrite (as well as other inorganic ions). However, nitrosamines could possibly be

TABLE 2-2. ESTIMATED CONSUMPTION OF NEUTRALIZING AND FILMING AMINES

Type of amine	Estimated 1978 consumption (metric tons)
Neutralizing amines	
Cyclohexylamine	3,200-3,600
Morpholine	1,800-2,200
2-Diethylaminoethanol	900-1,400
Methylpropylamine	400
All others	200
Total	6,500-7,800
Filming amines	
Octadecylamine	2,300
All others	200
Total	2,500

Sources: Stevens (1978) and MRI estimates.

introduced into water by resins used for deionization; samples of deionized water have been found to contain as high as 250 ng/liter of N-nitrosodimethylamine.

Other potential nitrosating agents are oxides of nitrogen from air. Nearly complete deaeration of boiler water is ordinarily employed to remove undesirable dissolved oxygen and carbon dioxide. These procedures would be expected to reduce greatly the concentration of dissolved nitrogen oxides in water. In addition, the boilers are operated at high pH (around pH 9 or 10) which further limits the formation and stability of nitrosamines. The classical secondary amine-nitrite reaction would not be expected to occur at this pH although the nitrosation of amines by oxides of nitrogen could occur rapidly.

Although there are limited data on the thermal degradation of nitrosamines in water, most of them are known to be thermally unstable, especially at temperatures in the range of 300°C. Temperatures of 250 to 300°C are attained in high-pressure boilers and sustained for relatively long periods of time.

Thus, eventual thermal decomposition of most nitrosamines would be expected under these conditions. Furthermore, there is evidence that the thermal stability of some amines is greatly reduced at the high pH values found in boiler waters.

Medium-Pressure Boilers

Boilers operating in the pressure range of 100 to 500 psi (maximum temperature about 240°C) utilize much different water treatment practice than higher pressure boilers. It is common for them to utilize a coordinated phosphate treatment system that allows operation with zero added caustic or to maintain the desired pH with very minor caustic additions. Sodium sulfite (or in some cases hydrazine) may be used as an oxygen scavenger. The use of sodium nitrate (at 200 to 400 ppm) to prevent caustic embrittlement is unknown to all the boiler specialists who were consulted in this study.

Hence, the occurrence of nitrosamines in moderate-pressure boilers is not likely to be attributable to reactions between organic amines and other chemicals intentionally added to manage these boiler water systems.

Low-Pressure Boilers

There are hundreds of thousands of relatively small, low-pressure boilers (25 to 200 psi, maximum temperature less than 190°C) in use for heating and process steam generation. The majority of these boilers are treated internally by the use of proprietary boiler water additives, which typically contain phosphates, sodium sulfite, and a sludge-conditioning polymer. None of the boiler compound suppliers contacted were aware of any additives which presently contain nitrates or nitrites. However, they did caution that some boiler additives formulated by some of the numerous, small boiler treatment supply firms could still incorporate nitrates and/or nitrites. The water used as feed presents another possible source of nitrate. Hence, the possibility of reaction between neutralizing amines and nitrates or nitrites is at least possible in some low-pressure boiler systems.

Hot-Water Boilers

So-called "hot-water boilers," used to circulate water to about 77°C for heating or to generate low-pressure steam at 10 to 12 psi with 100% condensate return, may employ sodium nitrite as a corrosion inhibitor. These systems are closed and require no makeup water since losses occur only if leaks are present. Chromate corrosion inhibitors are commonly used, but a combination of sodium nitrite and borate buffer is also widely employed. The water circulating systems do not use neutralizing or film-forming amines since the proper pH is maintained by the buffer system. The development of nitrosamines in hot-water heating systems is regarded as extremely unlikely.

Reports of Nitrosamines in Steam Emission from Boilers--

A recent report concerning a survey for N-nitroso compounds observed that small amounts (0.002 μg/g) of N-nitrosomorpholine were formed in the steam

condensate from boilers at a plant which produces chemicals for the rubber industry (Fan, Fajen, and Rounbehler, 1978). The authors were unable to ascertain exactly how the nitroso compound was formed, but they speculated that it was most likely formed by the transnitrosation reaction of morpholine with N-nitrosodiphenylamine produced at this plant and was detected at various locations within the plant. Morpholine is used at this plant as a neutralizing amine for the boilers and as a starting material for the manufacture of a vulcanization accelerator. N-Nitrosomorpholine was also detected at various locations throughout the plant in bulk samples and in air samples.

A total of 28 different plants were visited and sampled for N-nitrosamine contamination. Boiler steam condensate was sampled when nitrosamines were detected at other sites in the plant. N-Nitrosomorpholine was found in the steam condensate at only one plant; the condensate was collected from leaks in the steamline. Four of the other plants used morpholine in the boilers but had no N-nitrosomorpholine contamination. No samples of boiler "blow down" (the small fraction of water which is discharged from boilers for the purpose of preventing buildup of dissolved solids) were taken at any of the plants, and no record was made of the operating characteristics of the boilers. The authors observed that the nitroso compound exists as a contaminant in the morpholine itself and that this fact may account for its presence in the samples taken. However, nitrosamine formation via a transnitrosation reaction outside the boiler appears to be the most likely mechanism. Transamination can only occur when other nitrosamine contaminants are present.

Potential for Adverse Environmental Effects

Very little is known about the potential for environmental effects caused by the use of amines in boiler waters. However, over 2,700 metric tons of secondary amines, over 5,400 metric tons of primary amines, and over 900 metric tons of tertiary amines are consumed each year in these applications. The precise fate of these products is unknown. Evidently, some of them escape with steam emissions and some are discharged as boiler blowdown.

The discharged secondary amines would be subject to conversion to N-nitrosamines in the environment by a number of possible mechanisms. However, no information was found concerning the amounts or kinds of amines discharged from boilers. Also, no information was available that would conclusively indicate that boiler water discharges contain nitrosamines.

SECTION 3

VOLATILE CORROSION INHIBITORS

This section presents a definition of VCIs and describes specific compounds and their uses. Information concerning the market for VCIs is presented, and theories of the mode of action are discussed. The possibilities for nitrosamine formation and the potential for adverse environmental effects are also discussed.

DEFINITION OF VCIs AND THEIR FUNCTION

Every person contacted during this study and most literature references were in agreement about the meaning of volatile corrosion inhibitors or the equivalent term, vapor phase corrosion inhibitors. These terms mean a solid substance (rarely, a substance in solution) whose vapor pressure is sufficient in enclosed spaces to protect the metal surfaces upon which the volatilized substance condenses, i.e., inside a package, a closed storage area, or an automotive engine.

Uhlig (1971) in Corrosion and Corrosion Control described VCIs as "substances of low but significant vapor pressure, the vapor of which has corrosion-inhibiting properties" that are used to protect steel articles during shipping and storing.

Volatile and nonvolatile "atmospheric corrosion inhibitors" were discussed by Putilova et al. (1960). Nonvolatile atmospheric corrosion inhibitors are generally contact inhibitors whose actions are confined to the area where they are in contact with the metal surface. These can be nearly any of the compounds used in neutral aqueous solutions, especially alkali nitrites, e.g., sodium nitrite. Volatile atmospheric corrosion inhibitors are distinguished by their ability to protect while in the gaseous or vapor phase and are, therefore, termed "vapor phase inhibitors." Of the more than 100 different organic compounds tested up to about 1960, salts of amines and amino alcohols were the best inhibitors.

Wachter and Stillman (1952) defined a "vapor phase inhibitor" as a "compound which inhibits corrosion of metal parts in the presence of water and air (oxygen) because said compound possesses corrosion-inhibiting properties and is capable of vaporization under conditions of use with the resultant presence of these vapors in the vicinity of the metal." These authors recommended the use of a combination of two compounds, one of relatively high vapor pressure (e.g., diisopropylammonium nitrite, Dipan) to provide instant protection and one of lower vapor pressure (e.g., Dichan) to give prolonged protection.

Products called "vapor phase rust inhibitors," especially Dipan and Dichan, were developed by the Naval Research Laboratory for use in aqueous, nonflammable hydraulic fluids to prevent the rusting of ferrous metals in the vapor spaces of hydraulic systems. Brophy et al. (1951) described this development of "Hydrolubes," which were polymer-thickened, aqueous hydraulic fluids containing at least one glycol, especially ethylene glycol. The formulations described contained 1.6 to 1.7% Dipan. None of the "Hydrolubes" had proved satisfactory for prolonged use above 71°C. Zisman et al. (1951) patented "Hydrolubes" in which Dipan appeared as a "vapor-phase corrosion inhibitor."*

Wachter and Stillman (1952) patented water-glycol hydraulic fluids containing amine nitrites, preferably those of secondary amines such as Dichan or morpholine nitrite.

In 1951, Shell Development Corporation (Harman et al., 1951) patented an aqueous metalworking lubricant or coolant containing a mercaptan; some of these formulations contained 0.05 to 0.5% Dipan.

The use of amine nitrites as VCIs in the 1940's was quickly expanded to include packaging materials because desiccants and oils were often unsatisfactory for protecting military equipment and replacement parts during storage under all climatic conditions (e.g., at subzero temperatures, the viscosity of oils and greases prevent the operation of weapons). Use of the VCIs eliminated the tedious cleaning necessary when slushing compounds** were used (Baker, 1954).

COMPOUNDS USED AS VCIs

A large number of volatile organic compounds have been examined for use as VCIs. Most of the earlier published literature was by Japanese and European scientists (Putilova et al., 1960; Singh, 1976; Takahashi, 1975). The best VCIs for ferrous metal were found to be salts of dialkylamines and aminoalcohols. For nonferrous protection, benzotriazole and mercaptobenzothiazole were found to be very effective corrosion and tarnish inhibitors (Cotton and Scholes, 1967). Although a number of compounds has been patented as VCIs, only a few have been produced for commercial use in the United States. At the present time, the major VCI compounds are Dichan, substitutes for Dichan, and benzotriazole. Other amine salts such as dicyclohexylammonium benzoate, diisopropylammonium nitrite, and cyclohexylammonium carbonate have had limited use as VCIs in the United States. The physical properties of these compounds and their related nitrosamine derivatives are presented in Appendix A.

---

* Although the early "Hydrolubes" definitely contained the types of compounds recognized as VCIs in the literature, MRI was unable to find any such substance being used for that purpose today.

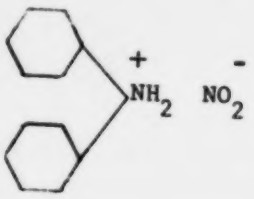
** Slushing compounds are petroleum-based materials, ranging from light oils to semisolids, containing inorganic or organic corrosion inhibitors (Campbell, 1948).

VCIs for Ferrous Metals

The protection of ferrous metals represents the largest fraction (over 90%) of the VCI market. At the present time, the market is dominated by Dichan and closely related compounds, but other compounds are known to be effective and have been used in the past.

Dichan--

Dichan is one of the most effective and widely used VCI compounds for ferrous metals. The substance is a white, crystalline salt with a very slight odor. It is volatile at room temperature with a vapor pressure of 0.0001 mm Hg at 21°C and is relatively nontoxic (Uhlig, 1971). It is produced commercially by the action of sodium nitrite on the water-soluble phosphate salt of dicyclohexylamine.



Dichan

Dichan is more suitable than Dipan for paper impregnation because it is less volatile (therefore, it lasts longer) and is less soluble (Baker, 1954).

Black and Wachter (1953) of the Shell Oil Company and the Shell Development Company, respectively, enumerated the benefits of using Dichan (these are also benefits of other VCIs of suitable vapor pressure):

1. Dichan gives excellent long-term storage protection.

2. Dichan will provide protection even if the container is damaged enough to allow entry of moisture vapor.

3. Surfaces of assemblies that cannot be reached by other means are protected by Dichan's vapor.

4. The application method is clean.

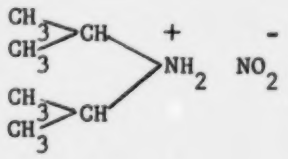
5. Costly and tedious degreasing operations are eliminated.

6. Protection is maintained under widely variable ambient conditions from arctic to tropical storage conditions.

7. Articles can be inspected easily.

Dipan--

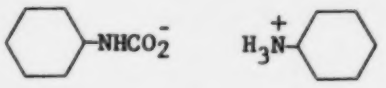
Dipan has been used as a VCI in the past, but there is no evidence of its use at the present time. It is a rather volatile compound with a vapor pressure of 0.012 mm Hg at 20°C and is therefore unsuitable for prolonged protection against atmospheric corrosion. It has a flash point of 40°F and thus would present a fire hazard. Another reason for its lack of use as a VCI is that although it protects steel, chromium and tin, it attacks copper, bronze, silver, aluminum, brass, antimony, Babbitt metal, cadmium, zinc, and lead (Putilova et al., 1960).



Dipan

Cyclohexylammonium Carbonate (CHC) and Other Carbonate Salts--

CHC is an effective VCI for ferrous metals (Lund, 1970). It has been produced commercially in the United States and Great Britain, but no production data were available. It can be used as a powder, but tablets and CHC-impregnated paper were available in 1964 (Anonymous, 1964). One reason for its current lack of use is that although it protects aluminum, zinc, chromium plate on steel tinplate, solder and soldered joints, it is very corrosive to copper, copper alloys, and magnesium (Uhlig, 1971). It also has a relatively high vapor pressure of 0.4 mm Hg at 25°C (Stroud and Vernon, 1975).



Cyclohexylammonium carbonate

Ethanolamine carbonate is another carbonate found to be an effective VCI (Uhlig, 1971) but is apparently not being used currently as a VCI in the United States.

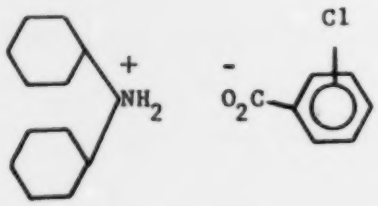
Benzoic Acid Salts--

Benzoic acid salts of diisopropylamine, dicyclohexylamine, ethanolamine, diethanolamine, triethanolamine, isopropylcyclohexylamine, N-ethylmorpholine, and naphthylamine have been tested and found to give "100% protective action toward steel" (Putilova et al., 1960). However, these compounds are apparently not used at the present time as VCIs in the United States.

Rosenfeld et al. (1972) reported that amine nitrobenzoates are much more effective than amine benzoates or amine nitrites as VCIs.

Alternatives--

Although Dichan was very recently the most widely used VCI, several VCI producers are changing to compounds that do not contain nitrite salts. The substitute compounds were not identified by the companies; however, patent literature and trade publications indicate that substituted benzoate salts (salts in which the anion contains a substituted benzoic acid group, e.g., a chlorobenzoic acid anion) are the compounds most likely to be used in place of nitrites. An example of a chlorobenzoate salt is:



Dicyclohexylammonium chlorobenzoate

VCIs for Nonferrous Metals

Benzotriazole is one of the most effective compounds used as a corrosion inhibitor for copper and other nonferrous metals such as chromium, nickel-silver alloys, and zinc-nickel alloys (Sherwin-Williams, 1976). It can be prepared directly by the action of nitrous acid on o-phenylenediamine and by the hydrolysis of an acylated or arylated benzotriazole. It is a white to off-white crystalline powder which melts at 96 to 97°C (Damschroder and Peterson, 1955).

Much lower levels (about 0.01 to 0.1 as much) of VCI are needed to protect copper than to protect steel (Schneider, 1978). For example, tissue paper carrying 2% by weight benzotriazole interleaved between copper mill sheets prevented tarnish for approximately 18 months. A brown wrapping paper coated with 0.43 g benzotriazole/m^2 and 10.8 g Dichan/m^2 protected copper and steel against water-saturated air containing 1% sulfur dioxide for 20 hr (Sherwin-Williams, 1976).

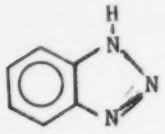
Most of the uses of benzotriazole for corrosion inhibition are not as VCIs. The compound has been used in antifreeze and engine coolants, cleaners, coatings, detergents, electrolytic processes, hydraulic and other functional fluids, metalworking processes, polishes and waxes, and water-circulating systems (Sherwin-Williams, 1976; Schneider, 1978). Table 3-1 shows the major uses of benzotriazole compounds (Davis et al., 1977).

TABLE 3-1. MAJOR USES OF BENZOTRIAZOLE COMPOUNDS

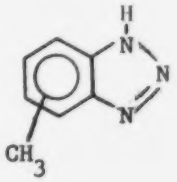
ANTI-CORROSION -	antifreeze compositions
	hot water heaters and associated pipes of iron, copper, and their alloys
	electric generator water cooling systems
	cleaning pastes and polishes
	impregnated protective paper (for packing, wrapping, and storage)
	dry cleaning fluids
	dishwasher detergent
	metal lacquers
	hydraulic and lubrication fluids
	electrolytic deposition (improves hardness and brightness)
ULTRAVIOLET STABILIZATION -	plastics, especially polyolefins
	other polymers, such as nylons and polyesters
	clear coatings
	paints and pigments
	oils
PHOTOGRAPHY -	antifoggants
	emulsion tint agent
	UV absorber/stabilizer
	thermographic photocopying processes

Source: Davis et al. (1977)

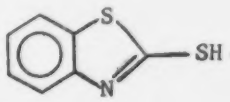
Competitors with benzotriazole (I) in some of these applications are tolyltriazole (II), 2-mercaptobenzothiazole (III), phosphonates, and chromates. The structures of compounds I, II, and III are show below:



I



II



III

Benzotriazole is taking over many corrosion inhibitor markets where the elimination of chromates is desired for environmental reasons (Schneider, 1978). There are a few uses of benzotriazole as a corrosion inhibitor in consumer products reaching the general public (e.g., hydraulic (brake) fluids and antifreezes). In addition, a product is marketed which consists of a sponge impregnated with benzotriazole to be placed unwrapped in a cutlery drawer or chest to protect silver (Schneider, 1978).

Alternatives--

No alternatives for benzotriazole and tolyltriazole as VCIs were specifically identified.

USES OF VCIs

VCIs are used for corrosion control of both ferrous and nonferrous metals. Over 90% of the amount presently being used is coated or impregnated in packaging and wrapping materials. VCIs are also currently being marketed as solid crystalline products in the form of pellets, tablets, and powders, which are often packaged in small permeable containers.

VCIs have many applications (Miksic, 1978; Kravik, 1978) in the packaging, shipping, and storage of a wide variety of items including:

Artifacts in museums
Ball bearings
Computers
Electrical transformers
Gasoline engines
Guns
Hearing aids
Marine electronic equipment
Molds
Motors
Piping
Process control devices
Propane tanks
Pumps
Tanks

VCIs are used in cartridges, tablets, or powder form to protect the following items:

Computers

Electrical equipment

Junction circuits

Process control equipment

Switch boxes

The major users of VCIs are discussed in the following paragraphs.

The Military

The principal use by the military and military contractors is for ordnance, including storage of weapons, combat vehicles, ammunition, maintenance tools, and equipment. Small parts are wrapped in VCI paper and sealed in containers. VCI crystals are placed in the cavities of aircraft engines and tanks in storage. The present military specification calls for an acceptable test to determine the effectiveness of compounds used as VCIs, but not their safety. Dichan and Dipan have been accepted by the military (Carroll, 1978).

The Automotive, Aircraft, and Tractor Industries

These industries are the largest users of VCI paper. The paper is used to protect small parts, e.g., ball bearings, electrical components, and gears, which are shipped overseas or stored for a period of months.

Steel and Copper Manufacturers

The steel industry uses VCI paper to wrap "black" plate, which is untinned steel, and tin plate produced for can companies. Stacks of cut steel plate (3 x 6 ft) on wooden pallets are wrapped with VCI paper. VCI paper containing benzotriazole is used by manufacturers of copper and other nonferrous products to prevent tarnish as well as corrosion.

Electrical and Electronic Equipment

VCI crystals in small permeable bags or cartridges are used in switch boxes and cavities of large electronic machinery located in areas having high humidity, warm temperature, or a salt water atmosphere (Kravik, 1978). Benzotriazole-treated paper is used to wrap reels of copper wire and electronic equipment. During subassembly storage, microwave components, electronic computer parts, typewriters, and radio and television circuit boards are protected by benzotriazole-coated papers. Manufacturers, such as Honeywell, Rockwell International, General Electric, Westinghouse, and General Motors also use VCI paper for the protection of metal parts and components.

Uses by the General Public

Currently the bulk of VCI paper and crystals is used by industry and not the general public. However, small amounts are used by individuals in the storage of tools, guns, and sterling silver (Miksic, 1977; Kravik, 1978).

MARKET INFORMATION

Based on information from numerous industrial sources, the total market for VCI products is estimated to be between $7 million and $8 million per year.* Approximately 311,000 kg/year of various chemicals are used as VCIs (see Table 3-2). Appendix D contains market information on VCIs and related products obtained from nonconfidential information submitted to EPA by manufacturers and importers as of January 1979. Until very recently, the market was dominated by Dichan,** but this product is rapidly being replaced by "nonnitrite" VCIs.*** By far the largest share of the market is represented by impregnated paper and other wrapping materials; apparently the market for impregnated paper is much greater than for other wrapping materials such as impregnated plastic films.

The size of the overall market has been stable for the past 4 to 5 years despite a reduction of VCI purchases by the military (Bell, 1978); this reduction has been offset by the growth of the VCI paper market.

The development of impreganted plastic wrapping material will probably be a significant factor affecting the future growth of the VCI market, in particular, the development of "cold seal" films of polyesters which are impregnated with VCI compounds is significant. These products will provide a transparent package which seals out moisture and gives corrosion protection. At the present time, these products are produced only by the Orchard Paper Company and sold as "Rapid Seal" (Van Winkle, 1978).

VCI-Impregnated Paper and Other Wrapping Materials

The market for VCI-impregnated paper is estimated by industry sources to be between $6 million and $7 million (Hutter, 1978). No production figures were available on the amount of each VCI compound used in this application.

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* A discussion of the overall market for volatile amines as corrosion inhibitors is presented in Appendix B.

** Boris Miksic, Chairman of the Volatile Corrosion Inhibitors Group (T-3A-4) of the National Association of Corrosion Engineers (NACE) in a letter to Norbert Page of NIOSH (January 1977) stated that he believed that the market for VCI compounds was "over 10 million pounds per year" (4,500,000 kg/year). Our contacts with manufacturers and users of these products have indicated that the market is less than one-tenth that size.

*** "Nonnitrite" VCIs are proprietary substitutes for Dichan (dicyclohexylammonium nitrite) in which the nitrite anion has been replaced with another anion, for example, a substituted benzoate anion.

TABLE 3-2. U.S. MARKET FOR VCI PRODUCTS, 1978

Compounds	Amount of VCI used (thousands of kg)	
	Impregnated paper and other wrapping materials	All other VCI applications
Dichan (dicyclohexyl-ammonium nitrite	95	14
Benzotriazole	30	0
"Nonnitrite" VCIs	170	2
Total	295	16

Source: MRI estimates.

However, the total market can be estimated from the average loading factor,* 11 g/m^2 (1 g/ft^2) and the average cost of VCI paper, 24¢/m^2 (20¢/yard^2); thus, over 27 million m^2 (30 million yard^2) of VCI paper is produced per year utilizing an estimated 295,000 kg of VCI chemicals. According to Hutter (1978) approximately one-third of this amount, or about 95,000 kg, is Dichan, and 11%, or about 30,000 kg, is benzotriazole. The remainder, about 170,000 kg, is estimated to be "nonnitrite" VCIs which have been used in place of Dichan (Hutter, 1978).

Daubert Chemicals, the main producer and user of the nonnitrite VCIs, considers the identity of the compounds and the amounts produced to be proprietary. However, the information in the patent literature and trade publications indicates that substituted benzoate salts of dicyclohexylamine and other fatty amines are the likely replacements for nitrite salts.

There are three major VCI paper companies: Daubert Chemicals, which is estimated to have 80% of the market; Ludlow Corporation, 15%; and Cromwell, 5%. Mead, Scott, and International paper companies are firms which buy small amounts of VCIs for more specialized products such as tissue for rolling sheet and excelsior for drums holding copper fittings (Schneider, 1978).

* The loading factor is the amount of VCI ordinarily used in the manufacture of impregnated paper.

VCI "Crystals"

Solid VCIs used for applications other than impregnated paper are referred to as "VCI crystals." The VCI crystal market is estimated to be slightly less than $1 million, which is equivalent to about 16,000 kg. Dichan represents about 85% of this market. The Olin Corporation is the major producer of Dichan crystals, which are marketed (as VPI® 260) by the Shell Chemical Company to small customers. The Alcon Company of New Orleans, Louisiana, also produces Dichan and is a major supplier to the military.

Benzotriazole

As indicated previously, the amount of benzotriazole used annually as a VCI in paper was estimated to be 30,000 kg (Hutter, 1978). This amount is consistent with an annual VCI paper production of 27 million m^2 and a loading factor of 1 g/m^2 (0.1 g/ft^2).

U.S. producers of benzotriazole are Sherwin-Williams, Eastman Kodak, Fairmount Chemical, Columbia Organic, Mobil Oil, and Sieflor (Appendix D).

Although Eastman Kodak sells benzotriazole through its Organic Chemicals and Photographic Chemicals Divisions, quite probably most of the benzotriazole is produced for captive use in photographic processes. The Organic Chemicals Division sells benzotriazole as a laboratory chemical in small packages through dealers. Only two companies, whose names were not revealed, have bought benzotriazole in large amounts. The Eastman Kodak representative did not recognize these two firms as users of corrosion-inhibiting chemicals (Van Sice, 1978).

Cross (1978), Vice President of Marketing at Fairmount Chemical Company, had no idea what the total U.S. production of benzotriazole is at the present time. Fairmount produces benzotriazole for photographic use but has been unable to penetrate the copper protection market held by Sherwin-Williams (Cross, 1978). Since Sherwin-Williams is the major producer and has a big share of the market, the U.S. International Trade Commission does not report benzotriazole production figures.

Schneider (1978), Product Manager for Triazole Products at the Sherwin-Williams Company, Chemical Division, estimated that world use of benzotriazole as a VCI was 68,000 kg (150,000 lb) in 1978. Complicating the estimate for U.S. consumption for that purpose is the possibility that a few companies may import benzotriazole to sell as a corrosion inhibitor. Although several foreign patents on benzotriazole as a corrosion inhibitor have been issued to American Hoechst Corporation, the company stated that none of the benzotriazole produced by the parent firm is imported for sale in the United States (Swift, 1978).

THEORIES OF THE MODE OF ACTION OF VCIs

Uhlig (1971) stated that the mechanism of VCI inhibition had "not been studied in detail" but that protection is apprently due to adsorption of a film on the metal surface that protects against water and/or oxygen.

Nitrite ion may be supplied by the volatile nitrites to passivate* the metal surface.

According to Rosenfeld et al. (1972), the effectiveness of a compound employed as a VCI depends on its saturated vapor pressure, its capacity to be adsorbed by the metal surface, and the presence of functional groups capable of passivating the metal surface.

Trabanelli and Zucchi (1976) and Trabanelli et al. (1967) have reviewed some of the theories which have been postulated concerning the mechanism by which VCIs protect against corrosion:

* The inhibitor saturates the atmosphere surrounding the metal surface, reducing the relative humidity at the metal-gas interface below a certain critical value.

* The adsorbed inhibitor renders the metallic surface hydrophobic, thereby preventing contact of the metal with moisture in the atmosphere.

* The inhibitor produces a strong electrical resistance on the metal surface which reduces the corrosion current.

* The inhibitor renders the metal surface alkaline causing the corrosion rate to become negligible.

* The inhibitor causes passivation of the metal surface by saturating the metal-gas interface with inhibitor and by polarizing the metal.

Very little information is available concerning the mechanism by which VCIs prevent corrosion. However, the following observations are significant. Black and Wachter (1953) stated that since Dichan (dicyclohexylammonium nitrite) is moderately water-soluble, its protection ability cannot be attributed to formation of a hydrophobic-adsorbed film. The pH of aqueous solutions of Dichan is near 7, so its action cannot be ascribed to the development of an alkaline pH. Dichan does not react detectably with oxygen, so it cannot be an oxygen scavenger. It is not especially hygroscopic, so its action cannot be that of a desiccant. Thus, the most reasonable mechanism for the VCI properties of Dichan is that its volatility serves as a means of transport to the metal surface where it contributes a nitrite ion (a recognized contact corrosion inhibitor) to condensed or adsorbed moisture on the metal surface (also in Wachter et al., 1951).

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* Passivation is a process in which the corrosion of a metal surface is inhibited by the formation of an insoluble compound by precipitation or reaction. Anions of weak acids, e.g., nitrite, chromate, benzoate, silicate, phosphate, and borate, form passivating films that stabilize the metal oxide coating (Uhlig, 1971).

The mechanism of "nonnitrite" VCIs is probably similar, except that the nitrite ion is replaced by a substituted benzoate ion.

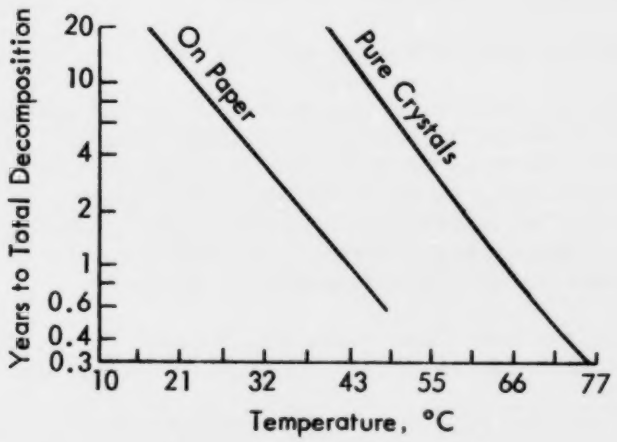
Benzotriazole is thought to form a 1:1 chemical complex with copper ions on the copper surface. This reaction results in the formation of a highly impermeable physical barrier layer 50 to 4,000 A thick (Sherwin-Williams, 1976).

POTENTIAL NITROSAMINE FORMATION IN DICHAN AND RELATED COMPOUNDS

The major VCI, Dichan, would be expected to be especially vulnerable to nitrosamine formation because it is a nitrite salt of a secondary amine. As described in Appendix C, "Nitrosamine Formation Potential," secondary amines are readily nitrosated by nitrous acid or nitrite under a wide variety of conditions. However, little published information was found concerning the conversion of Dichan to the corresponding nitrosamine.

An early experiment on the chemical and thermal stability of Dichan (Wachter et al., 1951) showed the possibility for nitrosamine formation. However, nitrosamines were not considered a serious hazard at that time, and the extent of nitrosamine content during decomposition studies was not measured.

Dichan was considered "remarkably stable"; a plot of years required for total decomposition versus temperature is presented in Figure 3-1.



Source: Wachter et al. (1951)

Figure 3-1. Thermal stability of Dichan.

For the study of the pure crystals, Dichan was sealed in glass tubes and stored at different constant temperatures for extended time periods. A variety of Dichan coated and impregnated papers were stored separately in waxed paper envelopes in a closed box at room temperature (about 72°F) for periods of 1 to 3 years.

The Dichan content of the crystals and the paper was measured on the basis of the nitrite content. The observed decreases in nitrite content could have been the result of the conversion of Dichan to the nitrosamine or the nitrate salt; however, no attempt to detect either of these products was reported.

Recent information obtained from an industrial source indicates that commercial Dichan contains "extremely low" amounts of nitrosamine. These amounts were not quantified but were said to be less than 1 ppm (Palm, 1978).

Nitrosamines from Benzotriazole

The preparation of benzotriazole and its derivatives is from the appropriately substituted o-phenylenediamine and nitrous acid. The photographic grade of benzotriazole is almost 100% pure, and the purity of the technical grade is 99.7 to 99.8% (Schneider, 1978).

Nitrosation might occur under the reaction conditions so that even when used without nitrite some nitrosamine could be present. However, Schneider (1978) stated that Sherwin-Williams had not been able to form the nitrosamine of benzotriazole under conditions such as varying the pressure, temperature, and nitrogen oxide concentration. However, the firm now recommends that sodium nitrite not be used with benzotriazole.

POTENTIAL FOR ADVERSE ENVIRONMENTAL EFFECTS

Little is known concerning the stability of VCI products in the environment. Dichan is known to be thermally unstable (Shell, 1972; Wachter et al., 1951). It is also known to be extensively decomposed by sunlight (20 to 50% decomposition in 60 days) (Wachter et al., 1951). As a VCI, Dichan enters the atmosphere where it is probably not a long-lived constituent because of its susceptibility to photolysis. However, no studies have been found concerning the nature or toxicity of its decomposition products.

Also, no reports have been found concerning the environmental effects or stability in the environment of Dichan substitutes or benzotriazoles.

As pointed out earlier, the biggest use of VCIs is in wrapping materials, especially impregnated paper. Archer and Wishnok (1976) detected N-nitroso-N,N-dibutylamine in a sample of "commercially produced, corrosion-resistant film of unknown composition." The concentration was estimated to be about 100 ppm. However, no indication was found that dibutylamine or any of its salts are actually used in products of this kind. Also, Wishnok stated that he did not know the commercial source of the sample, nor had their group done any further studies since the one which was published. The dibutyl nitrosamine was "tentatively" identified by a highly reliable analytical methodology, gas

chromatography-mass spectrometry. Archer (1978) stated that the supplier of the sample had responded that the identified compound was not one which could be expected.

Archer and Wishnok also prepared "a corrosion-resistant polyethylene film with a surface layer of morpholinium nitrite in an acrylic binder covered with a layer of latex." This film was subsequently (time unspecified) found to contain nitrosomorpholine. The nitrosamine concentration of a methylene chloride extract of the film was 90 ppm. These investigators also found 3,000 ppm of nitrosamine in an "unpurified" sample of the morpholinium nitrate which they prepared by a procedure in which carbon dioxide was bubbled through a mixture of morpholine and sodium nitrite in methanol.

Benzotriazole in contact with air, water, or sunlight is likely to be quite stable and persistent. However, the perceived potential for environmental contamination has been small, and the attention paid to it has been negligible (Davis et al, 1977).

SECTION 4

VOLATILE AMINES IN BOILER SYSTEMS

VCIs such as Dichan are not used in steam boilers; the compounds are too expensive and would probably be decomposed by the high temperatures (Wachter et al., 1951; Baker, 1954). However, a variety of volatile and nonvolatile amine compounds are employed to control corrosion in boilers. Also examined is the possibility that amines added to boilers might form nitrosamines through reaction with nitrites, nitrates, oxides of nitrogen, or any other nitrosating agent. The market for boiler water amines is also discussed.

This section of the report considers the current range of chemical practices used to manage boiler water in heating, process steam generation, and electrical power production.

BOILER WATER TREATMENT PRACTICES

The water used in boilers is treated by: (a) removing dissolved solids that would form adherent scale (softening or deionization); (b) removing dissolved gases, including oxygen and carbon dioxide; (c) adding alkali to maintain a desirable pH; and (d) introducing chemical agents that act as oxygen scavengers, neutralize carbon dioxide in the condensate, serve as passivators or corrosion inhibitors, and maintain precipitated sludge in a suspended condition. The sections which follow consider the water management practices that are typical for boilers operating from low pressure to super-critical pressures, with special emphasis upon the use of amines and any potential nitrosating agents.

The extent of pretreatment required for boiler feedwater and the type of compounds used to prevent scale formation, embrittlement, and corrosion are largely dictated by the type of boiler employed and its operating pressure. One convenient, though arbitrary, classification of boiler types is shown below (Hamer et al., 1961):

Boiler	Pressures (lb/in^2)	Maximum Temperatures (°C)
Low-pressure	Up to 200	190
Intermediate-pressure	200 to 500	240
High-pressure	500 to 2,000	335
Very high-pressure	2,000 to 3,209	375
Super-critical	Above 3,209	375

Feedwater Requirements

The requirement for feedwater purification becomes more stringent as the operating pressure increases. The concentration of dissolved solids in high-pressure and very high-pressure boilers must be held to much lower levels than for low-pressure or intermediate-pressure boilers. Table 4-1 gives the general characteristics typically required for feedwaters. Typical properties of the corresponding boiler waters are shown in Table 4-2.

Very large numbers of low-pressure boiler systems--these include relatively small heating systems and moderately sized industrial boilers--are operated with minimal pretreatment of the feedwater. Precipitation or exchange softening may be used, or proprietary boiler compounds may be added to the feedwater to achieve what is termed "internal treatment" in which all chemical treatment of the water is carried out entirely within the boiler system itself.

Internal treatment is widely used for the smaller and simpler boilers, such as the various types of shell boilers, but under certain conditions can also be used for watertube boilers. This type of treatment requires the maintenance of an adequate excess of sodium carbonate or phosphate in the boiler water to precipitate substantially all of the hardness in a form which will not adhere to boiler surfaces.

Most boilers designed to operate above 200 lb/in^2 utilize preliminary treatment of water to remove hardness and scale-forming impurities. For larger boilers, the use of demineralization or evaporation to provide high purity feedwater is widespread.

Oxygen Removal

After pretreatment, feedwater is treated to remove oxygen. The usual practice is to subject feedwater to physical deaeration by bringing it into contact with steam in the feed heater. An effective deaerator will reduce the dissolved oxygen to about 0.07 ppm (70 ppb) or less. Alternatively, the water may be held in the feedwater tank at 90 to 95°C for a period of 30 min to reduce dissolved oxygen to about 2 ppm. This type of oxygen removal is practiced on smaller, less elaborate boiler systems operating at 250 lb/in^2 or less.

Oxygen is further removed by the use of chemical reducing agents. The most important oxygen scavengers are sodium sulfite and hydrazine (Francis, 1962). Although other compounds have been reported in the literature, the boiler experts and operators interviewed in this study did not report using any other agents.

Sulfite--

Sodium sulfite reacts with oxygen to form sodium sulfate:

TABLE 4-1. RECOMMENDED CHARACTERISTICS OF BOILER FEEDWATER

Type of boiler	Recommended characteristics			Remarks
	Hardness (expressed as calcium carbonate) (ppm)	Alkalinity	Oxygen content	
Low-pressure (up to 200 lb/in^2)	< 20	Sufficient to give pH value of 9.0 or greater	May occasionally be necessary to reduce to below 0.14 ppm	Corrosion of feed systems is usually prevented by maintaining correct alkalinity in feedwater; corrosion of boiler is prevented by alkalinity control and by various mechanical arrangements for discharging gas into the steam space. Where oxygen content must be reduced, physical deaeration is used.
Medium-pressure (200-500 lb/in^2)	< 10	Sufficient to give pH value of 9.0	0.007-0.03 ppm	Good physical deaeration may be sufficient to give desired oxygen content; if not, sodium sulfite or hydrazine are added.
High-pressure (500-2,000 lb/in^2)	< 1	As for medium-pressure boilers	Nil	Good physical deaeration followed by continuous addition of sodium sulfite or hydrazine is essential.

Source: Hamer, Jackson, and Thurston, 1961.

TABLE 4-2. RECOMMENDED CHARACTERISTICS OF BOILER WATER[a]

Type of boiler	Recommended characteristics									Remarks
	Hardness (expressed as calcium carbonate) (ppm)	Sodium phosphate reserve (expressed as PO_4) (ppm)	Alkalinity	Alternative treatment chemicals to prevent caustic cracking: Sodium sulfate content	Sodium nitrate content	Phosphate content	Sodium sulfite excess (ppm) as such	Silica content (ppm) as such	Dissolved solids (ppm)	
Low-pressure (up to 200 lb lb/in^2)	≯5 when carbonate is used. ≯2 when phosphate is used.[b]	30-90[c] (where used)	Carbonate alkalinity should be > 200 ppm expressed as calcium carbonate and probably > 300 ppm.	Sufficient to give $Na_2SO_4/NaOH$ weight ratio > 2·5 and preferably > 3·0 in boiler water.	Sufficient to give ratio of $NaNO_3$ to total alkalinity (including phosphate if present) expressed as NaOH > 0·4 in boiler water.	Sufficient to give coordinated phosphate treatment, but rarely used in low-pressure boilers.	50-200 (where used)	Any	3,000-20,000	Dissolved solids depend on type of boiler.[d]
Medium-pressure (200-500 lb lb/in^2)	≯2[b]	30-90[c]	Sufficient to give pH value of 11 or more,[e] alkali content > 10% of dissolved solids.	As for low-pressure boilers.	As for low-pressure boilers.	Sufficient for coordinated phosphate treatment.	30-100[f]	200-50	10,000-3,000	Dissolved solids figures apply to watertube boilers and decrease as pressure increases. Suspended solids content of boiler water must also be taken into account. Figures for silica content appear to give complete safety from turbine blade deposits, but higher figures are often acceptable.
High-pressure (500-2,000 lb/in^2)	≯2[b]	30-90[c]	As for medium-pressure boilers.	As for low-pressure boilers.	As for low-pressure boilers.	As for medium-pressure boilers.	10-70[f]	50-10	3,000-1,000	Dissolved solids figures apply to watertube boilers, and decrease as pressure increases. Suspended solids content of boiler water must also be taken into account. Figures for silica content appear to give complete safety from turbine blade deposits, but higher figures are often acceptable.

a For recommended characteristics where internal treatment is used, see text.

b Measured by EDTA method.

c Typical values; reserve depends on possible rate of depletion and frequency of replenishment. Large quantities may be required where coordinated phosphate treatment is used.

d Figures are as follows:

Lancashire boiler	20,000 ppm
Watertube boiler	15,000 ppm
Economic boiler	4,000 ppm
Locomotive boiler	3,000 ppm

e Measured at atmospheric temperature.

f Sodium sulfite excess depends primarily on efficiency of initial mechanical deaeration (including that due to retention in hot feed tank). If mechanical deaeration is efficient and reliable, relatively low sodium sulfite excess only is required.

Source: Hamer, Jackson, and Thurston, 1961

$$2\ Na_2SO_3 + O_2 \longrightarrow 2\ Na_2SO_4$$

Sulfite is generally used as an oxygen scavenger for removal of oxygen from water that has been physically deaerated. Preliminary scrubbing to remove oxygen is essential, both to reduce the cost of chemicals and to prevent an undue buildup of dissolved solids content of the boiler water.

There are certain objections to the use of sodium sulfite as a deoxygenator, apart from the fact that it cannot be used without increasing the dissolved solids content of the boiler water. A more important objection is its liability to decompose at the higher boiler pressures to form hydrogen sulfide or sulfur dioxide. The fact that sodium sulfite does decompose in operating boilers seems to be established. As a general rule, sodium sulfite can be safely used as an oxygen scavenger in boilers working at pressures up to at least 1,000 lb/in^2, provided that the boiler water is alkaline and the concentration of sulfite is not above about 10 ppm (Na_2SO_3).

Hydrazine--

Hydrazine is a powerful reducing agent which reacts with dissolved oxygen under boiler conditions as follows:

$$N_2H_4 + O_2 \longrightarrow 2\ H_2O + N_2$$

It is thus capable of removing oxygen from the boiler water without increasing the dissolved or suspended solids content (Fletcher, 1958; Woodward, 1958). Hydrazine also decomposes under boiler conditions:

$$3N_2H_4 \longrightarrow 4NH_3 + N_2$$

The formation of ammonia from the hydrazine is regarded as advantageous in reducing the risk of corrosion by dissolved carbon dioxide in condensate.

As shown in the equation, one molecule of hydrazine is needed to remove one molecule of oxygen. In practice, however, a 100% excess of hydrazine in the feedwater is generally used so as to ensure rapid removal of the oxygen.

Prevention of Caustic Embrittlement--

Sodium nitrate was formerly added to boiler water to prevent caustic embrittlement.* Boiler experts were almost unanimous in pointing out that the occurrence of caustic embrittlement problems today is so rare that the embrittlement problem and chemical treatment to avoid it have all but disappeared (Thiedke, 1978; Johnson, 1978; Walters, 1978). Walters (1978) stated that nitrates have not been included in boiler compounds since about 1960. Thiedke

* Caustic embrittlement is the term used to describe the weakening of ferrous alloys which occurs when the alloys are under stress and exposed to caustic.

suspected that compounds offered by some of the smaller firms might still contain nitrates as a precautionary measure (Thiedke, 1978).

Coordinated phosphate treatment--Conditioning of carefully purified feedwater to maintain the desired pH at "zero-caustic" conditions is the most common means of avoiding caustic embrittlement. The technique is employed for boilers in the 500 to 1,800 lb/in^2 range (Fryling, 1966; Purcell and Whirl, 1942). This treatment involves adding sufficient acid sodium phosphate to the boiler water.

Chemical Treatment of Condensate Systems--

Condensate systems can be chemically treated to control corrosion damage caused by water and carbon dioxide. The treatment chemicals consist of neutralizing amines, filming amines, hydrazine, and, in many cases, ammonia.

Neutralizing amines--When condensate is to be used as feed for boilers, it is often necessary to reduce the pickup of iron so that the iron content is less than 0.01 to 0.1 ppm, depending on pressure. The pH level of the condensate should then be kept at about 9 by injecting a soluble neutralizing amine into the boiler feed or the steam line. The amine volatilizes with the steam and combines in the condensate with the carbon dioxide to form bicarbonates or carbonates. On returning to the boiler, the amine carbonates decompose to reform the amine and carbon dioxide. The process is to some extent then repeated. Losses occur through blowdown and leakage.

The compounds used for this purpose include ammonia, cyclohexylamine, morpholine, 2-diethylaminoethanol, methylpropylamine, and others (Hamer et al., 1961). The physical properties of these amines are presented in Appendix A. The use of ammonia has sometimes been considered objectionable since, especially in the presence of small amounts of oxygen, it can cause the corrosion of equipment made of copper or copper alloys. Ammonia is widely used, however, and corrosion of copper is prevented by maintaining the dissolved oxygen content of the feedwater at very low levels. Cyclohexylamine and morpholine, on the other hand, do not cause such corrosion, at least at the concentrations employed for preventing corrosion of ferrous metals.

The choice between ammonia and one or another of the organic amines depends on the quantities required and, hence, on the cost. The requirements depend on their relative basic strengths and volatilities. Under working conditions, very much smaller amounts of ammonia than of the organic amines are needed to raise the pH value of pure water by a given amount; furthermore, the price of a unit weight of ammonia is very much lower than that of either of the liquid amines. These advantages of ammonia are to some extent offset, however, by the fact that the volatility of ammonia in steam is so high that in some plants a large proportion will remain in the vapor phase and the desired effects of raising the pH value at the point where condensation first takes place will not occur unless large amounts of ammonia are used. Ammonia appears to provide the cheapest and most effective method of protecting condensate systems from corrosion, provided that the oxygen content is low so that attack on copper equipment can be disregarded.

The choice between cyclohexylamine and morpholine is difficult to resolve. Both amines appear to be equally stable substances; each amine decomposes under boiler conditions at temperatures above 370°C (Archibald et al., 1953). On the other hand, more recent work (Feitsma, 1958) suggests a decomposition temperature at 266°C for morpholine and 288°C for cyclohexylamine. Both have been used successfully (Rivers and Sonnett, 1950; Corey, 1947) in boilers operating at pressures up to about 1,500 lb/in^2. Their boiling points are close together--cyclohexylamine boils at 134°C and morpholine at 129°C--and their volatilities might accordingly be expected to be similar. Cyclohexylamine forms a constant boiling mixture (azeotrope) with water at 97°C, and this provides it a volatility in steam about 10 times greater than that of morpholine, which forms no azeotrope. Thus, morpholine condenses out more completely than cyclohexylamine at the point where condensation first takes place. However, cyclohexylamine is the stronger base of the two and is much more capable than morpholine of raising the pH level of condensate when it is present in equal quantities. The high volatility of cyclohexylamine also implies that the available reserve in the boiler water will be smaller than with morpholine for any given amine dose in the steam. Table 4-3 presents typical concentrations.

TABLE 4-3. QUANTITIES OF AMINES REQUIRED TO OBTAIN PARTICULAR pH VALUES IN PURE WATER

Amine	Conditions	Amount needed
Ammonia	CO_2 absent	0·2 ppm to give pH 9
Cyclohexylamine	CO_2 absent	1 ppm to give pH 9
	CO_2 present	2·3 parts per part of CO_2 to give pH 8·1 (corresponds to bicarbonate)
		2·0 parts per part of CO_2 to give pH 7·4
		1·4 parts per part of CO_2 to give pH 7
Morpholine	CO_2 absent	4 ppm to give pH 9
	CO_2 present	2·0 parts per part of CO_2 to give pH 7·4 (corresponds to bicarbonate)

Source: Hamer et al. (1961).

It appears from current operating experience that the maintenance of pH 9 in the condensate is adequate to ensure that steam/water systems will be protected against corrosion.

In estimating the overall requirements where part of the amine is recycled, allowance must be made for losses in unrecovered steam and also to some extent in blowdown. Sufficient amine must, therefore, be used not only to deal with fresh carbon dioxide entering the system, but also to make good those losses.

Filming amines--Certain straight-chain amines (containing 10 to 20 carbon atoms) have been found useful for controlling corrosion in steam-condensing systems in which the amines can form a protective adsorbed layer. This layer acts as a barrier between the metal and any liquid water, thus protecting the metal from attack by water containing dissolved oxygen or carbon dioxide. Octadecylamine (synthetic stearylamine, $C_{18}H_{37}NH_2$) is the material most commonly employed. Typically, the amine effects a reduction in corrosion of 80 to 95% with steam containing 4 to 60 ppm of carbon dioxide in the presence of oxygen at boiler pressures in the range 100 to 600 lb/in^2. It must be supplied continuously to the steam, for the film does not appear to be very persistent in operating conditions. The amine is either injected into the steam lines or is pumped directly into the boiler where the amine distills off with the steam. Feeding the amine directly to the boiler is reported to be inadvisable because of the risk of thermal decomposition. The amine is stable, however, to at least 425°C, and some authors have claimed stability at much higher temperatures, e.g., 535°C and above (Fryling, 1966).

PRESENT STATUS OF USAGE OF AMINES IN BOILERS

From discussion with boiler experts, it became clear that the chemical treatments currently employed with various types of boilers may differ from the standard methods reported in the literature (Webb, 1978; Thiedke, 1978). Therefore, the views and opinions of the sources consulted have been set forth as reflecting the more current commercial practices.

Major neutralizing amines currently used to treat boiler feedwaters are cyclohexylamine, morpholine, 2-diethylaminoethanol, and methylpropylamine (Hollingshad, 1978), and ammonia. Benzylamines are frequently mentioned in the literature as neutralizing amines for boilers, but Labine (1978) was not aware of any such commercial use of benzylamines.

Filming amines used to treat boiler waters or steam condensate lines directly include octadecylamine and other fatty amines containing at least 12 carbon atoms. These may also include secondary amines. For example, Armak Chemicals of Chicago produces the Ethomeen® series of secondary C_{12} to C_{18} amines that are sometimes used for boilers (Labine, 1978). The filming amines tend to foul pumps and strainers and other parts of a boiler system, and their popularity is declining (Hollingshad, 1978). However, if the neutralizing secondary amines had to be replaced with other substances, Labine (1978) indicated that filming amines would be used. Other experts believed that hydrazine and ammonia would be the more likely replacements for neutralizing amines.

The producers of boiler water additives usually formulate products with a mixture of amines having different volatilities. If the system covers relatively short distances, e.g., in a power plant where the boiler, turbine, and condenser are in close proximity, the amines used do not need to be highly volatile. In a refinery, where miles of piping may be employed, a product volatile enough to carry to the end of the system is needed. By applying the proper blend of high- and low-volatility amines, a product uniquely suited to the particular boiler system's geometry can be provided (Hollingshad, 1978).

Several contacts, including Hertz (1978) of Nalco Chemical Company, stated that nitrites are not normally added purposely to boilers. They are, however, used in closed heating or cooling systems, possibly with amines* (Labine, 1978; Hollingshad, 1978; Gabrelli, 1978). Nitrites might come in contact with boiler water because of some failure of a nitrite-containing closed system incorporated within a boiler system (Hollingshad, 1978). Webb (1978) stated that in modern-day power plant practice, the only possible use of nitrites would be as "boron nitrite" in the closed cycle cooling water (in place of sodium dichromate). Other industrial sources specified the use of sodium nitrite plus a borate buffer; and it is likely that such a combination is what Webb referred to as "boron nitrite."

Nitrates are also not intentionally added to boiler waters. They may rarely be present because a water softener might have been recharged with nitric acid (not a common practice) or because the plant is a meat plant (Labine, 1978). Nitrates have been used in the past as part of the "boilout" compound to clean down boilers as a precaution against caustic embrittlement (Murphy, 1978), but this method is now considered obsolete.

MARKET INFORMATION

About six volatile amines are in general use as boiler water additives (Hollingshad, 1978). These are listed below in Table 4-4 along with an estimate of their current annual consumption in boiler water. Appendix D contains available market information on these amines and related products obtained from nonconfidential information submitted to EPA by manufacturers and importers as of January 1979. A discussion of the overall market for amines as corrosion inhibitors is presented in Appendix B.

Calgon, Nalco Chemical Company, and Betz Laboratories are the largest suppliers of boiler water additives. Olin Water Services, Mogul Corporation, Dearborn Chemical Division, Chemed Corporation, and Drew Chemical Corporation are intermediate-sized companies; and there are a great many small companies. The eight named companies, however, probably represent 90 to 99% of the market for these materials (Hollingshad, 1978).

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* Boilers are considered open systems because of loss of steam or condensate and the drainage of "blowdown," the periodic removal of concentrated solids in the boiler.

TABLE 4-4. ESTIMATED CONSUMPTION OF SELECTED AMINES AS BOILER WATER ADDITIVES

Type of amine	Estimated 1978 consumption (metric tons)
Neutralizing amines	
Cyclohexylamine	3,200-3,600
Morpholine	1,800-2,200
2-Diethylaminoethanol	900-1,400
Methylpropylamine	400
All others	200
Total	6,500-7,800
Filming amines	
Octadecylamine	2,300
All others	200
Total	2,500

Sources: Stevens (1978) and MRI estimates.

About 40% of the total annual U.S. cyclohexylamine production is used for pH adjustment in boiler systems. It is sold directly to water treatment firms (Meek, 1978).

The total demand for morpholine in 1975 was about 11,000 metric tons. About 2,700 metric tons were used in corrosion inhibitors (of this quantity, 1,800 to 2,200 metric tons were used as neutralizing amines in boiler water - see Table 4-4); about 3,600 metric tons went into rubber chemicals; and about 900 metric tons went into each of the following categories: optical brighteners, waxes and polishes, alkylmorpholines, miscellaneous, and exports (Mjos, 1978). Several volatile boiler water amines are permitted by the U.S. Food and Drug Administration (FDA) to be "safely used in the preparation of steam that will contact food" (Federal Register, 1977). According to the FDA, steam in direct contact with food may contain less than or equal to 10 ppm cyclohexylamine, less than or equal to 15 ppm 2-diethylaminoethanol, less than or equal to 10 ppm morpholine, or less than or equal to 3 ppm octadecylamine (all

of these with the proviso that the steam is not to contact milk and milk products) (Code of Federal Regulations, Part 121.1088, 1976).

Less than 4,000 metric tons of 2-diethylaminoethanol was produced in the United States in 1976 (Mullins, 1978). 2-Diethylaminoethanol is also used in the preparation of medicinals and antimalarials.

Methylpropylamine has only recently been used as a boiler water neutralizing amine (Stevens, 1978).

POTENTIAL FOR NITROSAMINE FORMATION IN BOILERS

There is no experimental evidence to indicate whether or not nitrosamines are formed in boilers as a result of the addition of boiler-water amines. Most boilers are operated under conditions which would (a) limit the possibility for nitrosamine formation and (b) probably result in the destruction of any nitrosamine that might be formed. However, under certain circumstances, the possibility for nitrosamine formation is conceivable. These possibilities are discussed below.

Modern High-Pressure Boilers

Nitrates and nitrites are potential nitrosating agents for boiler water amines. However, neither nitrates nor nitrites are ordinarily added to boiler water (Hollingshad, 1978). For some high-pressure boilers, such as those used by electric utilities, high purity water is essential. As pointed out earlier, purification procedures include the careful removal of dissolved solids, including nitrates which occur in most untreated waters in the range 1 to 10 ppm. Some purification procedures require deionization of the water, and this process would remove nitrate and nitrite (as well as other inorganic ions). However, nitrosamines could possibly be introduced into water by resins used for deionization; samples of deionized water have been found to contain as high as 250 ng/liter of N-nitrosodimethylamine (Cohen and Bachman, 1978).

Other potential nitrosating agents are oxides of nitrogen from air. However, the presence of dissolved oxygen and carbon dioxide in boiler water is undesirable; therefore, nearly complete deaeration of boiler water is ordinarily employed. These procedures would be expected to reduce greatly the concentration of dissolved nitrogen oxides in the water.

A further detriment to the formation and stability of nitrosamines in boilers is the fact that they are operated at high pH values, around pH 9 or 10. The classical secondary amine-nitrite reaction would not be expected to occur at these pH values although the nitrosation of amines by oxides of nitrogen occurs rapidly at these pH values (see Appendix C).

Although there are limited data on the thermal degradation of nitrosamines in water, most of them are known to be thermally unstable, especially at temperatures in the range of 300°C. Temperatures of 250 to 300°C are attained in high-pressure boilers and sustained for relatively long periods of time.

Thus, eventual thermal decomposition of most nitrosamines would be expected under these conditions. Furthermore, there is evidence that the thermal stability of some amines is greatly reduced at high pH values such as found in boiler water (Lakings, 1980).

Medium-Pressure Boilers

Boilers operating in the pressure range of 100 to 500 psi (maximum temperature about 240°C) utilize much different water treatment practices than higher pressure boilers. This type of boiler commonly utilized a coordinated phosphate treatment system to allow operation with zero-added caustic or to maintain the desired pH with very minor caustic additions. Sodium sulfite (or in some cases hydrazine) may be used as an oxygen scavenger. Since the introduction of welded boiler construction (about 1930) and stress relief of the boiler parts before use, caustic embrittlement has become virtually a problem of the past. The practice of using sodium nitrate (at 200 to 400 ppm) to prevent caustic embrittlement is unknown to all the boiler specialists who were consulted in this study.

Hence, the occurrence of nitrosamines in moderate-pressure boilers is not likely to be attributable to reactions between organic amines and other chemicals intentionally added to manage these boiler water systems.

Low-Pressure Boilers

There are hundreds of thousands of relatively small, low-pressure boilers (25 to 200 psi, maximum temperature less than 190°C) in use for heating and process steam generation. The majority of these boilers are treated internally by the use of proprietary boiler water additives, which typically contain phosphates, sodium sulfite, and a sludge-conditioning polymer. The occurrence of caustic embrittlement is so rare that none of the boiler compound suppliers were aware of any additives which presently contain nitrates or nitrites. However, they cautioned that some boiler additives formulated by some of the numerous, small boiler treatment supply firms could still incorporate nitrates and/or nitrites. The water used as feed presents another possible source of nitrite. Hence, the possibility of reaction between neutralizing amines and nitrates or nitrites is at least possible in some low-pressure boiler systems.

Hot-Water Boilers

So-called "hot-water boilers," used to circulate water to about 77°C for heating or to generate low-pressure steam at 10 to 12 psi with 100% condensate return, may employ sodium nitrite as a corrosion inhibitor. These systems are closed and require no makeup water since losses occur only if leaks are present. Chromate corrosion inhibitors are commonly used, but a combination of sodium nitrite and borate buffer is also widely employed. The water circulating systems do not use neutralizing or film-forming amines since the proper pH is maintained by the buffer system. The development of nitrosamines in hot-water heating systems is regarded as extremely unlikely.

Reports of Nitrosamines in Steam Emissions from Boilers

A recent survey of N-nitroso compounds observed that small amounts (0.002 μg/g) of N-nitrosomorpholine were found in the steam condensate from boilers at a B. F. Goodrich plant which produces chemicals for the rubber industry (Fan, Fajen, and Rounbehler, 1978). The authors were unable to ascertain exactly how this nitrosamine (or other nitrosamines detected at the plant) was formed. In the report, they speculated that it was most likely formed by the transnitrosation reaction of morpholine with N-nitrosodiphenylamine. The latter compound, a vulcanization retarder, is produced at this plant and was detected at various locations within the plant in amounts ranging from 47 to 50,000 μg/g in bulk samples and from 0.3 to 47 $\mu g/m^3$ in air samples.

Morpholine is used at this plant as a starting material for the manufacture of bismorpholine carbamylsulfenamide, an accelerator. The N-nitrosomorpholine was detected at various locations throughout the plant, ranging from 0.002 μg/g in steam condensate to 731 μg/g in scrappings from staircases, and from 0.07 to 6.8 $\mu g/m^3$ of the compound in air samples. The authors also observed that this compound exists as a contaminant in morpholine (0.8 μg/g) and this fact may account for its presence in the samples taken.

Fajen (1979) of NIOSH provided additional information concerning these studies. Morpholine was also used as a neutralizing amine for the boilers at the B. F. Goodrich plant. Many of the steam lines at the plant were leaking, and these leaks were the source of their samples. The program team was concerned that the steam emissions might contain N-nitrosomorpholine as a result of the known contamination of the morpholine starting material. However, this was subsequently shown to be unlikely because it was not detected in the steam emissions from boilers at other plants which used morpholine as a neutralizing amine.

As part of this program, 28 different plants were visited for the purpose of detecting N-nitrosamine contamination. Steam condensate samples were examined only when nitrosamines were detected elsewhere in the plants. No samples of boiler blowdown were taken at any of the plants, and no record was made of the operating characteristics of the boilers. The foremen of the boiler rooms were contacted in order to determine whether morpholine was used as a boiler additive. Bulk samples of the boiler additives were also taken for analysis for the presence of morpholine and N-nitrosomorpholine. Some of the plants used morpholine; for example, five plants serving the rubber industry used morpholine in the boilers. However, of all the plants visited, only the B. F. Goodrich plant was found to contain this nitroso compound in the steam condensate from boilers.

At the present time, it is not possible to rule out morpholine in the boiler as a source of N-nitrosomorpholine contamination. However, nitrosamine formation via a transnitrosation reaction outside of the boiler appears to be the most likely mechanism. Transnitrosation can only occur when other nitrosamine contaminants are present.

Additional studies are required to clarify this situation; additional steam condensates from boilers using morpholine (and other amines) should be examined using sampling techniques which would preclude transnitrosation. Also, similar examinations should be made of boiler blowdown.

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APPENDIX A

PHYSICAL PROPERTIES OF VCIs, BOILER WATER AMINES AND RELATED COMPOUNDS[a/]

a/ Unless otherwise noted, the physical properties of these compounds were obtained from the Merck Index (9th Edition, 1976, published by Merck and Company, Inc., Rahway, New Jersey) or the Dictionary of Organic Compounds (4th Edition, 1965, published by Oxford University Press, New York).

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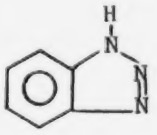
BENZOTRIAZOLE

Chemical Formula: $C_6H_5N_3$

Structure: 

Molecular Weight: 119.12

Description: White powder

Melting Point: 98.5°C

Boiling Point: $bp_{15} = 204°C$; $bp_{2.0} = 159°C$

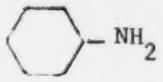
Density: $d_{25}^{100} = 1.19$

Solubility: Soluble in alcohol, toluene, chloroform, DMF.
Slightly soluble in water.

Source: Sherwin-Williams (1976)

CYCLOHEXYLAMINE

Chemical Formula: $C_6H_{13}N$

Structure: 

Molecular Weight: 99.17

Description: Liquid, strong fishy amine odor.

Melting Point: solidifies at -17.7°C

Boiling Point: $bp_{760} = 134.5°C$

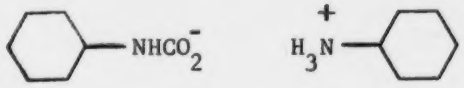
Density: $d_{25}^{25} = 0.8647$

Refractive Index: $n_D^{25} = 1.4565$

Solubility: Completely miscible with water and common organic solvents.

CYCLOHEXYLAMMONIUM CARBONATE

Chemical Formula: $C_{13}H_{26}N_2O_2$

Structure: 

Molecular Weight: 242.36

Description: White crystals.

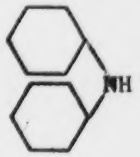
Vapor Pressure: 0.394 mm Hg at 25°C

Solubility: Soluble in water, methanol and ethanol.

Source: Stroud and Vernon (1952).

DICYCLOHEXYLAMINE

Chemical Formula: $C_{12}H_{23}N$

Structure: 

Molecular Weight: 181.31

Description: Liquid, faint fishy odor

Melting Point: solidifies at -0.1°C, mp ~ 20°C

Boiling Point: $bp_{760} = 256°C$

Flash Point: 110°C

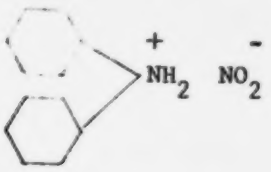
Density: $d_{25}^{25} = 0.9104$

Refractive Index: $n_D^{25} = 1.4823$

Solubility: Slightly soluble in water; soluble in organic solvents

DICYCLOHEXYLAMMONIUM NITRITE (DICHAN)

Chemical Formula: $C_{12}H_{24}N_2O_2$

Structure: 

Molecular Weight: 228.33

Description: White crystalline solid

Melting Point: 178 to 180°C
154°C (technical product)

Vapor Pressure: 1.2×10^{-4} mm Hg at 21.0°C

Solubility: Slightly soluble in water; soluble in methanol, ethanol

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Sources: Wachter et al. (1951); Wolfe and Temple (1948).

DIETHANOLAMINE

Chemical Formula: $C_4H_{11}NO_2$

Structure: $(HOCH_2CH_2)_2NH$

Molecular Weight; 105.14

Boiling Point: bp_{760} = 268.8°C

Melting Point: mp = 28°C

Flash Point: 300°F

Density: d_4^{20} = 1.09664

Dipole Moment: 2.81

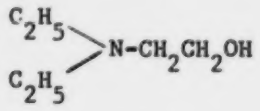
Viscosity: V^{30} = 351.9 cp

Solubility: miscible with water, methanol, acetone, very soluble in ethanol, slightly soluble in benzene, ether.

Source: Weast (1976) and Toxicology Data Bank File.

2-DIETHYLAMINOETHANOL

Chemical Formula: $C_6H_{15}NO$

Structure: 

Molecular Weight: 117.19

Description: Liquid

Boiling Point: $bp_{760} = 163^{\circ}C$

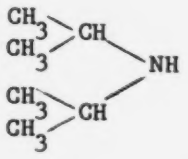
Density: $d^{25} = 0.8800$

Refractive Index: $n_D^{25} = 1.4389$

Solubility: Soluble in water, alcohol, ether, benzene.

DIISOPROPYLAMINE

Chemical Formula: $C_6H_{15}N$

Structure: 

Molecular Weight: 101.19

Description: Liquid, characteristic odor, strongly alkaline

Boiling Point: 84°C

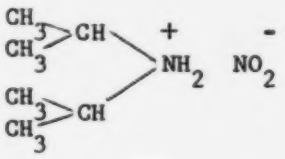
Density: $d^{22} = 0.722$

Solubility: Soluble in water, alcohol

DIISOPROPYLAMMONIUM NITRITE (DIPAN)

Chemical Formula: $C_6H_{16}O_2N_2$

Structure:



Molecular Weight: 148

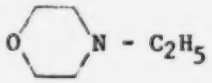
Melting Point: 136 to 137°C

Vapor Pressure: 0.012 mm Hg at 20°C

Sources: Wolfe and Temple (1948); Putilova et al. (1960).

N-ETHYLMORPHOLINE

Chemical Formula: $C_6H_{13}NO$

Structure: 

Molecular Weight: 115.18

Boiling Point: bp_{763} = 138-139°C

Freezing Point: fp = 32°C

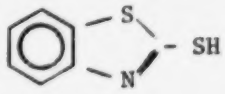
Melting Point: mp = -63°C

Solubility: Soluble in water, alcohol, ether, acetone, benzene.

Source: Toxicology Data Bank File.

MERCAPTOBENZOTHIAZOLE

Chemical Formula: $C_7H_5NS_2$

Structure: 

Molecular Weight: 167.25

Density: $d^{25} = 1.42$

Melting Point: mp = 180.2 - 181.7

Solubility: Solubility at 25° (g/100 ml) in alcohol: 2.0; ether: 1.0; acetone: 10.0; benzene: 1.0; soluble in alkalies and alkali carbonate solutions.

METHYLPROPYLAMINE

Chemical Formula: $C_4H_{11}N$

Structure: $CH_3CH_2CH_2NHCH_3$

Molecular Weight: 73

Description: Liquid with fishy odor

Boiling Point: 62 to 64°C

Density: $d^{17} = 0.7204$

Solubility: Soluble in water

MORPHOLINE

Chemical Formula: C_4H_9NO

Structure:

Molecular Weight: 87.12

Description: Colorless hygroscopic liquid, with characteristic amine odor.

Melting Point: -4.9°C

Boiling Point: $bp_{760} = 128.9°C$; $bp_6 = 20.0°C$

Flash Point: 38°C

Density: $d^{20} = 0.994$

Vapor Density: $d_4^{20} = 1.007$

Vapor Pressure: 7.0 mm Hg at 20°C

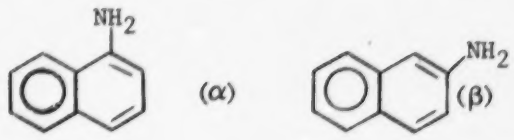
Refractive Index: $n_D^{20} = 1.4540$

Solubility: Miscible with water, acetone, benzene, ether, castor oil, methanol, ethanol, ethylene, and glycol.

Source: Mjos (1978).

NAPHTHYLAMINE[a/]

Chemical Formula: $C_{10}H_9N$

Structure:  (α) (β)

Molecular Weight: 143.19

	α	β
Boiling Point:	bp_{760} = 300.8°C	bp_{760} = 306.1°C
Melting Point:	mp = 50°C	mp = 113°C
Density:	d_{25}^{25} = 1.1229	d_{4}^{98} = 1.0614
Solubility:	Soluble in 590 parts water, freely soluble in alcohol and ether.	Soluble in hot water, alcohol, ether.

Source: Weast (1976).

a/ The International Agency for Research on Cancer has published an evaluation of the carcinogenicity of 1-naphthylamine (α) and 2-naphthylamine (β): "Epidemiological studies have shown that occupational exposure to 2-naphthylamine, either alone or when present as an impurity in other compounds, is strongly associated with the occurrence of bladder cancer. There is no doubt that 2-naphthylamine is a human bladder carcinogen." (IARC, 1973.)

"Exposure to commercial 1-naphthylamine containing 4-10% 2-naphthylamine is strongly associated with bladder cancer. It is not possible on present evidence to decide whether 1-naphthylamine free of the 2-isomer is carcinogenic to man." (IARC, 1973.)

N-NITROSODIBUTYLAMINE [a/]

Chemical Formula: $C_8H_{18}N_2O$

Structure: $O = N - N\begin{matrix}\diagup CH_2-CH_2-CH_2-CH_3 \\ \diagdown CH_2-CH_2-CH_2-CH_3\end{matrix}$

Molecular Weight: 158.28

Description: Pale yellow liquid

Boiling Point: $bp_{760} = 234° - 237°C$

Density: $d^{20} = 9.009$

Solubility: 12% soluble in water at room temperature, miscible with hexane, dichloromethane, and other organic solvents.

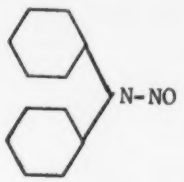
Source: MRI, (1977).

a/ The International Agency for Research on Cancer has published an evaluation of the carcinogenicity of N-nitrosodibutylamine: "There is sufficient evidence of a carcinogenic effect of N-nitrosodi-n-butylamine in several experimental animal species. Although no epidemiological data were available, N-nitrosodi-n-butylamine should be regarded for practical purposes as if it were carcinogenic to humans." (IARC, 1978.)

N-NITROSODICYCLOHEXYLAMINE

Chemical Formula: $C_{12}H_{22}N_2O$

Structure:



Molecular Weight: 210.36

Description: Crystalline needles

Melting Point: 107°C

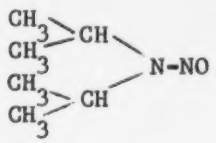
Solubility: Water solubility 0.0015 g/100 ml

Source: Druckrey et al. (1967); Wolfe and Temple (1948)

N-NITROSODIISOPROPYLAMINE

Chemical Formula: $C_6H_{14}N_2O$

Structure:



Molecular Weight: 130.22

Boiling Point: 96°C at 28 mm Hg

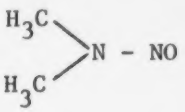
Solubility: Water solubility, 1.3 g/100mℓ

Source: Druckrey et al. (1967).

N-NITROSODIMETHYLAMINE [a/]

Chemical Formula: $C_2H_6N_2O$

Structure:



Molecular Weight: 74.09

Boiling Point: $bp_{760} = 154°C$

Density: $d_4^{20} = 1.0048$

Refractive Index: $n_D^{20} = 1.4368$

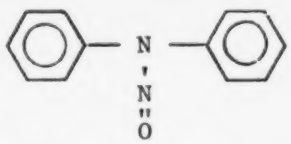
Solubility: Miscible with water, methylene chloride, vegetable oils; soluble in all common organic solvents and in lipids; very soluble in alcohol, ether.

Source: Toxicology Data Bank File.

a/ The International Agency for Research on Cancer has published an evaluation of the carcinogenicity of N-nitrosodimethylamine: "There is sufficient evidence of a carcinogenic effect of N-nitrosodimethylamine in many experimental animal species. Similarities in its metabolism by human and rodent tissues have been demonstrated. Although no epidemiological data were available, N-nitrosodimethylamine should be regarded for practical purposes as if it were carcinogenic to humans." (IARC, 1978.)

N-NITROSODIPHENYLAMINE

Chemical Formula: $C_{12}H_{10}ON_2$

Structure: 

Molecular Weight: 198

Description: dark-brown solid

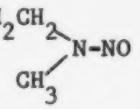
Melting Point: 63 - 66°C

Solubility: Soluble in warm EtOH, Warm C_6H_6

Source: NCI, 1979.

N-NITROSOMETHYLPROPYLAMINE

Chemical Formula: $C_4H_{10}ON_2$

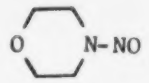
Structure: 

Molecular Weight: 102

Boiling Point: 175°C

N-NITROSOMORPHOLINE[a/]

Chemical Formula: $C_4H_8N_2O_2$

Structure: 

Molecular Weight: 116.1

Description: Yellow Crystals

Melting Point: 29°C

Boiling Point: $bp_{747} = 224\text{-}225°C$

$bp_6 = 96°C$

Solubility: Miscible in water; soluble in organic solvents

Source: IARC (1978).

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a/ The International Agency for Research on Cancer has published an evaluation of the carcinogenicity of N-nitrosomorpholine: "There is sufficient evidence for a carcinogenic effect of N-nitrosomorpholine in several experimental animal species. Although no epidemiological data were available, N-nitrosomorpholine should be regarded for practical purposes as if it were carcinogenic to humans." IARC (1978).

OCTADECYLAMINE

Chemical Formula: $C_{18}H_{37}NH_2$

Structure: $CH_3(CH_2)_{17}NH_2$

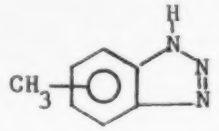
Molecular Weight: 269

Description: Liquid

Boiling Point: $bp_{2.5}$ = 172 to 173°C

TOLYLTRIAZOLE

Chemical Formula: $C_7H_7N_3$

Structure: 

Molecular Weight: 133.16

Description: off-white granules

Density: $d_{25}^{100} = 1.13$

Solubility: Slightly soluble in water; soluble in methanol and other alcohols.

Source: Sherwin-Williams (1976).

TRIETHANOLAMINE

Chemical Formula: $C_6H_{15}NO_3$

Structure: $(HOCH_2CH_2)_3N$

Molecular Weight: 149.19

Boiling Point: bp_{760} = 335.4°C

Density: d_4^{20} = 1.1242

Flash Point: 365°F

Melting Point: mp = 21.2°C

Refractive Index: n_D^{20} = 1.4852

Viscosity: V^{25} = 590.5 cp

Source: Weast (1976).

APPENDIX A - REFERENCES

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APPENDIX B

THE MARKET FOR AMINES AS CORROSION INHIBITORS

A recent report by Frost and Sullivan entitled The Corrosion Inhibitors Market estimated that 1976 expenditures for corrosion control goods and services were $10.5 billion (Anonymous, 1978a). Three classes of corrosion inhibitors were considered. The water-soluble inhibitors market in 1976 was said to be $204 million; the oil-soluble inhibitors market, $92 million; and the vapor phase inhibitors market, $16.3 million.

A 1975 survey by the National Association of Corrosion Engineers (NACE, 1976) estimated that total expenditures for corrosion control were $9.7 billion and vapor phase inhibitor purchases were $12.4 million.

The NACE survey queried its membership about the amounts spent for corrosion protection, including the chemical inhibitors divided into the categories: water-soluble, oil-soluble, and "vapor phase" inhibitors. Table B-1 presents the survey's results for the latter category.

Miksic (1978), Chairman of the NACE task committee on volatile corrosion inhibitors (T-3A-4), suspected that in most cases, boiler-water chemicals, not VCIs, are what the NACE membership perceives as "corrosion inhibitors, vapor phase type" (Table B-1). Miksic recognizes that a semantics problem exists and is attempting to clarify the definition of these corrosion inhibitors within NACE.

Attempts were made to obtain the types and quantities of the compounds used as indicated in Table B-1 with emphasis on obtaining data from industries which appear to use over 78% of the vapor phase inhibitors, i.e., the chemical and petrochemical industries, and the petroleum production and refining industries. The author of the NACE report was contacted (Castleberry, 1979) but could not provide these data and believed that they were not available.

The Charles H. Kline and Company, Inc., of Fairfield, New Jersey, will soon publish a multiclient study entitled "Refinery, Gas Conditioning, and Pipeline Chemicals, 1978." According to a Kline representative (Rosenberg, 1979), this 2-1/2 year survey will include information on chemical compositions, quantities, market share, dollar volume, typical usage, and market forecasts. The survey will include refinery boiler water chemicals and corrosion inhibitors used in pipelines. According to the company's brochure (Kline, 1979), most of the information in the survey appears to deal with dollar volumes, not pounds, of chemicals, and categories of products, not specific compounds; the only specific compounds pertinent to this study that were noted in an outline of this study are morpholine, monoethanolamine,

TABLE B-1. ESTIMATED USE OF VAPOR PHASE CORROSION INHIBITORS BY INDUSTRY

Industry	Amount spent on "corrosion inhibitors, vapor phase types" Dollars (millions)	Percent[a/]
Chemical and petrochemical industries	4.012	32.4
Petroleum production	3.199	25.8
Petroleum refining	2.482	20.0
Electrical utilities	0.396	3.2
Engineering and/or construction	0.281	2.3
Crude oil pipeline transmission	0.263	2.1
Natural gas transmission	0.237	1.9
Pulp and paper industry	0.208	1.7
Government	0.158	1.3
Research	0.114	0.9
Metals industry	0.105	0.8
Nuclear power industry	0.079	0.6
Equipment manufacturing industries	0.057	0.5
Gas utilities	0.003	0.0
Water utilities	0.000	0.0
Communications	0.000	0.0
Other industries	0.789	6.4
	12.383	

a/ Figures may not total 100% due to rounding.

Source: NACE, 1976.

and diethanolamine; of these, only morpholine is used extensively as a boiler water additive. The absence of other volatile amines from the outline confirms our opinion that the "vapor phase types" of corrosion inhibitors listed by NACE (Table B-1) as used by the "petroleum refining," "natural gas transmission," and "crude oil pipeline transmission" industries are indeed boiler water additives, and not VCIs.

A partial summary of the information compiled by Kline and Company is presented in Table B-2.

A comparison of the estimates made by Kline and by NACE shows some important discrepancies (Table B-3). As indicated in the table, major differences occur in estimates of the amounts of corrosion inhibitors used: (a) to treat water in refinery operations and (b) in petroleum and gas transmission operations.

Perhaps the major reason for these discrepancies is that each estimate was based to a large extent upon personal knowledge and opinion obtained via interviews. Another problem is the fact that boiler water amines are commonly sold to the user at a price which includes in-plant corrosion control service (Ward, 1979).

The size of the discrepancies in dollar volume obtained in these two extensive and detailed surveys provides an indication of how time-consuming and difficult it would be to obtain reliable information concerning the quantities and types of chemicals used. Rosenberg (1979), who is participating in the Kline and Company survey, estimated that a minimum of 200 interviews, including some on-site visits, would be required in order to obtain even a rough estimate of the chemicals used and their amounts. He also stated that the end users of the inhibitors would not be very helpful mainly because they do not know the composition of the products they use.

Frost and Sullivan, Inc., New York, New York, published a report in 1978 entitled "Corrosion Inhibitors Market." According to their catalog, this report provides a forecast of the corrosion inhibitor market, including markets for boilers, oil well, and refinery operations. In this report, as well as the Kline and Company survey, the emphasis appears to be placed on dollar amounts of products sold and not pounds of chemicals used.

Personal Interviews

Knowledgeable representatives of the following chemical and petrochemical industries were contacted concerning volatile amines used as corrosion inhibitors.

TABLE B-2. ESTIMATED U.S. SALES OF CHEMICALS AND FORMULATED CHEMICAL SPECIALITIES IN REFINING, GAS CONDITIONING, AND PIPELINE TRANSMISSION, 1977[a/]

Use category	Millions of dollars
Refining	
Water treatment	
Corrosion inhibitors	$ 30
Other chemical products	52
	82
Processing	
Corrosion inhibitors	15
Other chemical products	16
Total	$113
Gas conditioning	
Ethanolamines	$ 30
Other chemical products	27
Total	$ 57
Pipeline transmission	
Petroleum	
Corrosion inhibitors	$ 15
Other chemical products	18
	$ 33
Gas	
Corrosion inhibitors	$ 15
All other	2
	$ 17
Total	$ 50
Grand total	$220

Source: Kline (1979)

a/ Excludes service.

TABLE B-3. COMPARISON OF NACE AND KLINE SURVEYS CONCERNING CORROSION INHIBITORS (MILLIONS OF DOLLARS)

	Kline estimate (for 1977)	NACE estimate (for 1975)
Refining		
Water treatment	30	2.4 ("vapor phase types")
Processing	15	-
Total	45	32
Pipeline transmission		
Petroleum	15	9.4 (0.26 "vapor phase types")
Gas	15	4.9 (0.24 "vapor phase types")
Total	30	14.3

Sources: Kline (1979); NACE (1976).

* Union Carbide, Tarrytown, New York
* Du Pont, Wilmington, Delaware
* Dow Chemical, Midland, Michigan
* Standard Oil Company, Sugar Creek, Missouri
* Amoco Research, Naperville, Illinois
* Shell Oil Company, Houston, Texas
* Gulf Oil Company, Houston, Texas
* Texaco, Inc., White Plains, New York

In general, these representatives know of no large-scale uses by their industry group of volatile amines as corrosion inhibitors except in boiler operations. They also were not knowledgeable of exactly what compounds were contained in the boiler water chemicals, other than that they were neutralizing or film-forming amines.

APPENDIX B - REFERENCES

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APPENDIX C

REVIEW OF POSSIBLE NITROSAMINE FORMATION REACTIONS OF VCIs AND BOILER WATER AMINES

The most likely possibility as a source of nitrosamines from VCIs and boiler water amines is the nitrosation of secondary amines. All of the VCI amines presently used are secondary amines, and about one-third of the neutralizing amines are secondary amines. However, cyclohexylamine and octadecylamine are primary amines which represent major fractions of the market for neutralizing and filming amines, respectively (see text, p. 34). In addition, 2-diethylaminoethanol is a tertiary amine which represents 10 to 20% of the market for neutralizing amines (see text, p. 34).

Edwards et al. (1978) have reported that "contrary to popular belief, not only secondary amines, but also primary and tertiary amines can all yield N-nitroso compounds."

Discussed below are the reactions which could produce nitrosamines from VCIs and boiler water amines.

Nitrosation of Secondary Amines

The classic method for producing nitrosamines is the interaction of secondary amines with nitrous acid; in practice, the method consists of acidifying a solution containing a nitrite salt and a secondary amine (Mirvish, 1975).

$$R_1R_2NH + NO_2^- + H^+ \longrightarrow R_1R_2N\text{-}NO + H_2O$$

In the acid-catalyzed nitrosation of secondary amines, nitrite is usually first converted to nitrous acid, which in turn is converted to an active nitrosating species: nitrogen (III) oxide (N_2O_3), nitrous acidium ion ($H_2NO_2^+$), nitrosyl cation (NO^+), nitrosyl thiocyanate (ON-NCS), or nitrosyl halide (NOX) (Olajos and Coulston, 1978). The nitrogen (III) oxide moiety ($N_2O_3 \rightleftharpoons NO_2 \cdot NO$) is the active nitrosating agent in the pH range 1 to 4; at the dilute acidic conditions that are encountered in the environment, this moiety is likely the one which nitrosates secondary amines (Fine, 1979).

The N-nitrosation of secondary amines is usually very slow at neutral or alkaline pH because of the low equilibrium concentration of nitrous anhydride. However, in the presence of formaldehyde, chloral (Keefer and Roller, 1973), or some metal ions, appreciable nitrosation can occur even at pH 6 to 11 (Fine, 1979).

In pure buffered aqueous systems, dimethylamine in the presence of nitrite was not nitrosated at pH values above 5.0; however, in sterilized soil and sewage samples, nitrosation was observed to occur at pH values as high as 7.7 (Mills and Alexander, 1976).

Nitrosation can take place by other reactions; for example dimethyl- and diethyl-nitrosamines are evidently formed in air by the reaction of nitrogen oxides with the secondary amines (Fine and Rounbehler, 1976). The nitrosating agent can be nitrogen (II) oxide (NO), nitrogen (IV) oxide ($NO_2 \rightleftharpoons N_2O_4$), or nitrogen (III) oxide (N_2O_3), (Edwards et al., 1978). Nitrogen (II) oxide (NO) itself has been shown to be a poor nitrosating agent (Challis and Kyrtopoulos, 1976). However, nitrosation in the presence of NO and air proceeds readily, presumably because of oxidation of some of the NO to NO_2 and the formation of N_2O_3 from NO and NO_2. Nitrosation by N_2O_3 and N_2O_4 proceeds rapidly at room temperature in aqueous solution at a pH in the range of 6 to 14. The reactions are very much faster than those with acidified nitrite (Challis et al.,

Pitts et al. (1978) have reported studies of the nitrosation of diethylamine in air containing ambient levels of NO and NO_2. Diethylamine is rapidly nitrosated in the dark but is subsequently destroyed by sunlight.

Fan et al. (1978) have recently shown that certain C-nitro compounds[a/] can readily nitrosate secondary amines to form N-nitroso compounds. C-nitro compounds are widely used as pesticides, bactericides, coloring agents, drugs, and perfumes (Fine, 1979). The reaction occurs rapidly at neutral and alkaline pHs, but alkaline conditions are the most favorable (Fine, personal communication, 1978).

Transnitrosation of aliphatic secondary amines has also been demonstrated to occur (Singer et al., 1978). Transnitrosation is the transfer of the nitroso group of one N-nitrosamine to another amine to form a different N-nitrosamine.

$$R_1R_2N\text{-}NO + R_3R_4NH_2 \longrightarrow R_3R_4N\text{-}NO + R_1R_2NH_2$$

Many transnitrosation reactions are known to take place in strong aqueous acid (pH 1.5) and the reactions are catalyzed by nucleophiles such as thiocyanate or halide ion. Some secondary amines are more easily nitrosated by this reaction than others; for example, morpholine can apparently be readily nitrosated by a variety of nitrosamines (Fine, 1978). Also, some nitrosamines appear to be stronger nitrosating agents than others (Singer et al., 1978).

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a/ A C-nitro compound is a compound in which a nitro group (NO_2) is attached to an aliphatic carbon atom.

The nitrosation of secondary amines by microorganisms at pH values above 5.0 has been reported by several investigators (Archer et al., 1978). Rate enhancements of from 12- to 49-fold have been observed when dihexylamine was nitrosated at pH 3.5 in the presence of bacteria and yeast cells; a non-enzymatic mechanism is proposed (Archer et al., 1978).

Very little has been reported concerning the potential transformation to nitrosamines of secondary amines used as VCIs or boiler water additives. N-nitrosomorpholine has been detected on one occasion in the steam emissions from boilers (see text, p. 36). However, the morpholine added to the boiler is not believed to be the source of the nitrosamine. Dichan, the nitrite salt of a secondary amine, apparently can be at least partially transformed to the corresponding nitrosamine (see text, p. 21).

Nitrosamines from Primary and Tertiary Amines

Although the nitrosation of secondary amines has been studied extensively, there are relatively few publications concerning the formation of nitrosamines from primary and tertiary amines.

The nitrosation of primary amines yields monoalkylnitrosamines which are highly unstable (Olajos and Coulston, 1978). However, small quantities of secondary amine N-nitroso compounds are also formed in this reaction via a mechanism which is not well understood (Fine, 1979).

Tertiary amines react with nitrous acid to yield amine type N-nitroso compounds. Erroneous reports to the contrary have persisted for over 100 years (Fine, 1979). The reaction involves a nitrosative dealkylation; an alkyl group must first be cleaved oxidatively to yield the secondary amine, which then becomes nitrosated. The mechanism of this reaction has been discussed by Lijinsky et al. (1972).

No reports were found concerning the formation of nitrosamines from primary or tertiary amines used as boiler additives.

APPENDIX C - REFERENCES

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APPENDIX D

MARKET INFORMATION ON SELECTED COMPOUNDS USED FOR CORROSION INHIBITION[1/]

Compound (CASRN)[2/]	Manufacturer	1977 Production (lb)	Importer
Benzotriazole syn: IH-Benzotriazole (95-14-7)	Fairmount Chemical Co.	0 to 1,000	No
	Columbia Organic Chemicals	0 to 1,000	No
	Agfa-Gevaett	0	Yes
	The Sieflor Corp.	"small manufacturer"	Yes
	Sherwin Williams Chemicals	"manufacturer"	No
	Mobil Oil Corp.	0 to 1,000	Yes
	Unknown[3/]	0	No
Cyclohexylamine syn: Cyclohexanamine (108-91-8)	Drew Chemical Corp.	10,000 to 100,000	Yes
	Mobay Chemical Corp. New Martinsville, W.Va.	"manufacturer"	No
	Pittsburgh, Penn.	not a manufacturer	Yes
	American Hoechst Corp.	0	Yes
	Thorson Chemical Corp.	0 to 1,000	Yes
	The Sieflor Corp.	"small manufacturer"	Yes
	Sandoz Colors & Chemicals - N. J.	0	Yes
	Unknown[3/]	0 to 1,000	Yes

(continued)

APPENDIX D (continued)

Compound (CASRN)[2/]	Manufacturer	1977 Production (lb)	Importer
Cyclohexylamine (continued)	I. Schneid Inc., Ga.	"manufacturer"	No
	Machemco Inc.	"manufacturer"	No
	Chemical Exchange Co., Inc.	100 million to 500 million[4/]	No
	E. I. du Pont Victoria, Tex.	1,000 to 10,000	No
	Orange, Tex.	10,000 to 100,000	No
	Virginia Chemicals Inc., Portsmouth	"manufacturer"	No
	C. Itoh and Co., Inc.	0	Yes
	Abbott Laboratories	"manufacturer"	No
Dibenzylamine syn: Benzenemethanamine, N-(phenylmethyl)- (103-49-1)	Uniroyal Chemical Division, Uniroyal Inc.	0 to 1,000	No
	Miles Laboratories Inc., Sumner Division	"manufacturer"	No
	Hexcel Corp., Specialty Chemicals Division	"manufacturer"	No
	The Ames Laboratories Inc.	0 to 1,000	No
Dicyclohexylamine syn: Cyclohexanamine, N-cyclohexyl- (101-83-7)	Kodak Park Division	0 to 1,000	No
	BASF Wyandotte Corp.	0	Yes
	American Hoechst	-	Yes
	Virginia Chemicals, Inc. Portsmouth	"manufacturer"	No
	Koch Chemical Co.	not a manufacturer	Yes

(continued)

APPENDIX D (continued)

Compound (CASRN)[2/]	Manufacturer	1977 Production (lb)	Importer
Dicyclohexylamine (continued)	Abbott Laboratories	"manufacturer"	No
Dicyclohexylammonium Nitrite	Olin Corp.	10,000 to 100,000	No
syn: Cyclohexanamine, N-cyclohexyl-, nitrite (3129-91-7)	Northern Instruments Corp.	1,000 to 10,000	No
Diethylamine	Ashland Chemical Co. International Division	0	Yes
syn: Ethanamine, N-ethyl- (109-89-8)	Pennwalt Corp.	"manufacturer"	No
	BASF Wyandotte Corp.	10,000 to 100,000	Yes
	Air Products & Chemicals Inc. Pace, Fla.	"manufacturer"	No
	St. Gabriel, La.	"manufacturer"	No
	Uniroyal Chemical Division, Uniroyal Inc.	0[4/]	Yes
	Virginia Chemicals, Inc. Portsmouth	"manufacturer"	No
2-Diethylaminoethanol	Penwalt Corp.	"manufacturer"	No
syn: Ethanol, 2-(diethylamino)- (100-37-8)	Haven Chemical	"small manufacturer"	No
	Union Carbide Corp.	"manufacturer"	No
	Alcolac Inc.	"manufacturer"	No
	SST Corp.	0 to 1,000	Yes
	The Ora Corp.	1 million to 10 million	No
	Proctor Chemical Co., Inc.	1 million to 10 million	No

(continued)

APPENDIX D (continued)

Compound (CASRN)[2]	Manufacturer	1977 Production (lb)	Importer
2-Diethylaminoethanol (continued)	ICI Americas Inc.	1,000 to 10,000	Yes
	Unknown[3]	"small manufacturer"	No
Diisopropylamine syn: 2-propanamine N-(1-methyleth-yl)- (108-18-9)	Pennwalt Corp.	"manufacturer"	No
	Union Carbide Corp.	"manufacturer"	No
	Air Products & Chemicals Inc.	"manufacturer"	No
	ICI Americas Inc.	not a manufacturer	Yes
	Unknown[3]	0 to 1,000	No
Methylpropylamine syn: 2-butanamine (13952-84-6	BASF Wyandotte Corp.	0	Yes
	American Hoechst Corp.	0	Yes
	E. I. du Pont de Nemours & Co.	1 million to 10 million[4]	No
	Virginia Chemicals, Inc., Portsmouth	"manufacturer"	No
Morpholine (110-91-8)	Henkel, Inc.	0 to 1,000	Yes
	Henley & Co., Inc.	not a manufacturer	Yes
	Union Carbide Corp.	0	No
	BASF Wyandotte	100,000 to 1 million	Yes
	ABC Compounding Co., Inc.	1,000 to 10,000	No
	American Bio-Synthetics Corp.	"small manufacturer"[4]	No
	Jefferson Chemical Co., Inc. Port Neches, Tex.	"manufacturer"	No
	Conroe, Tex.	"manufacturer"	No

(continued)

APPENDIX D (concluded)

Compound (CASRN)[2/]	Manufacturer	1977 Production (lb)	Importer
Morpholine (continued)	Unknown[3/]	"small manufacturer"	No
N-Nitrosodiisopropylamine	Kodak Park Division	0	No
syn: 1-propanamine, N-nitroso-n-propyl- (621-64-7)	The Ames Laboratories Inc.	0 to 1,000	No
Octadecylamine	Armak Industrial Chemicals		
syn: 1-octadecylamine (124-30-1)	McCook, Ill.	"manufacturer"	No
	Morris, Ill.	"manufacturer"	No
	Ashland Chemical Company Oakland, Calif.	0	No
	Mapleton, Ill.	100,000 to 1 million	No
	I. Schneid Inc., Ga.	"manufacturer"	No
	Machemco Inc.	"manufacturer"	No
	General Mills Chemicals Inc.	"manufacturer"	No
	Unknown[3/]	1,000 to 10,000	Yes
Tolyltriazole	American Hoechst Corp.	not a manufacturer	Yes
syn: 1H-Benzotriazole, methyl (29385-43-1)	Sherwin Williams Chemicals	"manufacturer"	No

1/ Based on nonconfidential information submitted to the EPA by manufacturers and importers as of January, 1979.

2/ Chemical Abstracts Service Registry Number.

3/ Link between information and company has been claimed to be confidential.

4/ Chemical is manufactured and consumed on site.